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Monday, August 3, 2015
8:00 AM - 10:00 AM

Introduction/Plenary

Location: Missouri
Session Chair(s): Joan Redwing, Luke Mawst

8:30 AM - 9:15 AM
GIANT CRYSTALS OF NAICA: THE SCIENCE BEHIND THE BEAUTY
Invited
Juan M. García
Consejo Superior de Investigaciones Científicas, Armilla (Granada), Spain

GIANT CRYSTALS OF NAICA: THE SCIENCE BEHIND THE BEAUTY
Juan Manuel García-Ruiz
Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Granada, Spain

Crystals are everywhere in our day life, but only in a very few cases do they reveal themselves as the large polyhedra that have fascinated mankind since remote times. Even rarer is to find colossal crystals other than those dreamed up in literature and comic masterpieces. However, there are exceptions. The Cave of Giant Crystals in the Naica mine (Mexico) is one of the most amazing displays of mineral beauty ever created by nature. In addition to the colossal columnar crystals of gypsum (CaSO_4 \cdot 2H_2O), which in some cases exceed eleven meters in length and one meter in thickness, the scenery developed by the crystalline beams of moonlight luster going through the darkness of the cave, from the floor to the ceiling, is a unique example of harmony based on crystal symmetry. At the same time, deciphering the formation mechanism of these crystals is a fascinating challenge. In this lecture I will review the nucleation and growth of gypsum crystals as the scientific basis for the formation of this remarkable phenomenon of mineralization.

References:

9:15 AM - 10:00 AM
AlGaN-BASED TECHNOLOGY: STATE-OF-THE-ART AND REMAINING CHALLENGES
Invited
Zlatko Sitar
North Carolina State University, Raleigh, NC

AlGaN alloys are the building blocks of deep UV optoelectronics and high-power devices. It has been demonstrated that the highest crystalline quality AlGaN films with high Al content are obtained on AlN single crystal substrates. Recently, UV LEDs emitting at 265 nm with output powers exceeding 80 mW and high reliability, as well as low-threshold, optically pumped lasers emitting at wavelengths between 230-280 nm have been demonstrated. These results demonstrate the advantages of using AlN substrates for this technology. Despite the encouraging results, challenges in strain management and management of point defects pose the remaining limitations of this technology. Pseudomorphic AlGaN films with dislocation densities lower than 1E3 cm\(^{-2}\) have been achieved, sustaining compressive stresses with thicknesses exceeding 3 µm. If relaxation is not essential for a given application, relaxation schemes can be avoided altogether in favor of pseudomorphic AlGaN films on AlN. As single-crystal AlN substrates have low dislocation densities, of the order of 1E3 cm\(^{-2}\), it is unrealistic to expect sufficient strain accommodation through dislocation bending of pre-existing dislocations. This makes misfit dislocation nucleation an essential mechanism in the relaxation of these films. Composition and strain relaxation in high Al content AlGaN layers grown by MOCVD on AlN substrates will be discussed with respect to the substrate miscut. It was found that the nucleation of misfit dislocations in AlGaN layers depends on the presence of either macrosteps or bilayer steps on the growth surface. As misfit controls the surface step morphology, it plays a crucial role in misfit dislocation nucleation and alloy critical thickness. Following these results, dislocation densities below 105 cm\(^{-2}\) have been obtained in these films for Al content higher than 60%.

These low dislocation densities allowed for a systematic approach to the identification and control of compensating point defects that affect n-type conductivity. This approach has been guided by a first-principles-based database that combines point defect data to predict defect concentrations and significant optical transitions for defect identification. This is currently guiding the development of the Fermi level control scheme for point defect management that has allowed for the achievement of high free carrier concentrations in high Al content AlGaN films.

The talk will discuss MOCVD processes for control of AlGaN composition and heteroepitaxy, approaches to control strain, point defects, and doping in this material, and implications of this technology for further development of UV optoelectronic and electronic devices.
SYNTHESIS, CRYSTAL GROWTH, AND STRUCTURAL CHARACTERIZATION OF NOVEL ZINTL PHASES OF AS, SB AND BI WITH THE D-METALS

Invited
Svilen Bobev
University of Delaware, Newark, DE

The crystal chemistry of the intermetallic compounds containing metals with different electronegativities presents a combination of diverse and complicated bonding patterns and unique metal-metal interactions. As part of an ongoing effort to better understand the structure-property relationships in such intermetallics containing d- and/or f-elements, we focused our attention on the ternary systems A-M-As, A-M-Sb and A-M-Bi (A = alkali, alkaline-earth metals, and/or rare-earth metal; M = Mn, Zn, Cd). Recent experimental work carried out by our group led to the discovery of several new classes of transition metal based compounds. Common threads in the structures of all of these are the M-centered tetrahedra of As, Sb or Bi, respectively, which are interconnected through shared corners or edges to form chains, ribbons, or layers with complex topologies. These systems present a case where a strikingly delicate balance between the packing efficiency (size effects) and the valence electron concentration (electronic effects) governs the stability of a particular arrangement over another. The structural relationship between these and some well-known structures with two-dimensional layers or three-dimensional four-connected nets will be discussed as well.
IN SITU OBSERVATION OF PHASE SEPARATION AND HIERARCHICAL MICROSTRUCTURE OF KXFE2-YSE2 SINGLE CRYSTALS

Yong Liu, Qingfeng Xing, Warren E. Straszheim, Jeff Marshman, Pal Pedersen, Thomas A. Lograsso

1 Ames Laboratory, Ames, IA, 2 Carl Zeiss Microscopy, LLC, Ion Microscopy Innovation Center (IMIC), Peabody, MA, 3 Carl Zeiss Microscopy, LLC, Thornwood, NY

As solid-state phase transformations occur, materials exhibit rich microstructures depending on the heat treatment conditions, for example quenching temperatures, heating and cooling rates, and pressure [1,2]. The mechanical [3], magnetic [4], transport and superconducting properties [5] of materials can be significantly changed by tuning microstructures upon heat treatment. The KxFe2-ySe2 single crystals exhibit an iron vacancy order-disorder transition at Ts~270 °C [6,7]. Below Ts two spatially separated phases, a minority/superconducting phase and a majority/iron vacancy-ordered phase. However, the nature of this phase separation is not well understood. Here, temperature dependent SEM images provide compelling evidence that phase separation corresponds to a nucleation and growth process rather than a spinodal decomposition. The superconducting phase is the remnant of high temperature phase after iron vacancy order-disorder transition. Three-dimensional (3D) spatial distribution of superconducting phase in the iron vacancy ordered matrix was revealed by using focused ion beam scanning electron microscopy (FIB-SEM). Our results clearly show that superconducting phase forms a hierarchical structure. Understanding the formation of this hierarchical structure not only can guide the synthesis of bulk superconductors in the future, but also greatly enrich our knowledge about the interplay between phase separation and solid-state phase transformations.

References

11:15 AM - 11:30 AM
SINGLE CRYSTAL GROWTH OF Fe-BASED HIGH TEMPERATURE SUPERCONDUCTORS
chenglin zhang
Huazhong University of Science & Technology, Wuhan, China
Since the discovery of Fe-based high temperature superconductors on 2008, they have been subjected to heavy study. However, most of investigation are carried out on one or two such types of families. Many others are barely touched upon due to the unavailability of single crystals. Usually, Alkali metals (Na,K) and toxic Arsenic are been involved in the synthesis, making the high temperature growth notorious difficult. By our custom-designed functional furnaces and home-made recipe, our crystals can reach up 2'' with mass up to 8 g, in contrast to the regular crystals with mm scale in size and mg weight in mass. I will introduce the ways how they made.

11:30 AM - 11:45 AM
STRUCTURE, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF NOVEL GdNi0.85Al0.85 COMPOUN
NAGALAKSHMI RAMAMOORTHI, RASHID T P, NALLAMUTHU SENGODAN, ARUN K, MARRIAN REIFFERS, IVAN CURLIK, SERGEJ ILKOVIC, SEKAR M
1National Institute of Technology, Tiruchirappalli, India, 2Faculty of Humanities and Natural Sciences, Presov University, Presov, Slovakia, Slovakia, 3Faculty of Humanities and Natural Sciences, Presov University, Presov, Slovakia, 4Material Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

STRUCTURE, MAGNETIC AND MAGNETOCALORIC PROPERTIES OF NOVEL GdNi0.85Al0.85 COMPOUND
1Department of Physics, National Institute of Technology, Tiruchirappalli 620 0015, India, 2Faculty of Humanities and Natural Sciences, Presov University, Presov, Slovakia, 3Material Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India
The magnetic refrigeration based on magnetocaloric effect (MCE) has attracted a great deal of interest for its energy-efficient and environment-friendly behavior, compared to the common vapor-cycle refrigeration technology. We synthesized novel polycrystalline GdNi0.85Al0.85 compound by arc melting method and its crystal structure, magnetic properties, magnetocaloric effect and refrigerant capacity have been investigated. We find that the GdNi0.85Al0.85 crystallizes in hexagonal ZrNiAl type structure (space group Pm2; major phase) and in cubic GdAl type structure (space group Fd; minor phase). The lattice parameters a and c were determined to be 7.0143 and 3.9647 Å respectively, by the Rietveld technique using Fullprof program, consistent with those given in Ref.1. A second-order magnetic transition from the ferromagnetic to the paramagnetic state with no thermal or magnetic hysteresis is confirmed at T = 46K. The maximum values of magnetic entropy change of GdNi0.85Al0.85 for a field change of 0-9T is 9.15 J kg⁻¹K⁻¹. A large refrigerant capacity 514.43 J/kg, under a field change of 0-9T with no hysteresis loss is the advantage of GdNi0.85Al0.85 compound.

Reference

Keywords: Rare-earth intermetallic compound, X-ray diffraction, Magnetocaloric effect
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11:45 AM - 12:00 PM
TUNING OF CRYSTALS ON ATOMIC SCALES IN ORDER TO UNDERSTAND COLLECTIVE PHENOMENA
Athena S. Sefat
Oak Ridge National Laboratory, Oak Ridge, TN
This talk focuses on crystal structural features that give clues for the causes of collective phenomena such as antiferromagnetism or superconductivity. Our research involves Fe-based material preparations in single crystal forms, and their characterization using a range of bulk and local methods. In order to present an overview of our recent work, a few of our studies from 2015 will be briefly highlighted, in order to demonstrate the role of crystal structure for understanding materials' properties.
* This work was primarily supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.
The synthesis method may provide an economical advantage for bulk crystal growth of many metal halide compositions. Improvement over previous performance of CsCaI₃:Eu with prior reports of 8 boules. Poorer performance was correlated to the boules with wall nucleated grains. The measured energy resolution of the 662 KeV photopeak from a 137Cs source ranged between 6 & 8% (FWHM/Centroid) across all boules. Poorer performance was correlated to the boules with wall-nucleated grain structures. The present results are a significant improvement over previous performance of CsCaI₃:Eu with prior reports of 8-16% energy resolution at 662 KeV. The demonstrated synthesis method may provide an economical advantage for bulk crystal growth of many metal halide compositions.

Eu doped SrI₂ (Eu:SrI₂) single crystal have been energetically investigated as a next-generation gamma-ray scintillator with high light yield and energy resolution. Eu:SrI₂ scintillator crystals with strong hygroscopic nature have been grown by the Vertical Bridgman (VB) method using a quartz ampoule. On the other hand, we developed a modified micro-pulling-down (µ-PD) method with a removable chamber in order to grow single crystals of halide materials at higher growth rate than the VB method. We reported the results of crystal growth and scintillation properties of halide scintillator crystals as represented by CeBr₃, Ce:LaBr₃ and Eu:SrI₂ using the modified µ-PD method. However, the modified µ-PD method does not allow us to grow a bulk single crystal. Therefore, we developed a novel VB method using the µ-PD furnace with the removable chamber suitable for hygroscopic halide materials. The carbon crucible is designed for the growth of 2 inch Eu:SrI₂ single crystal. SrI₂ and EuI₂ powders (> 4N, APL Japan) were used as a starting material and the mixed powder with nominal composition of (Sr₁₋ₓEuₓI₂), (Eu₂%:SrI₂) was set into the crucible. Undoped SrI₂ single crystal grown by the µ-PD method used as a seed crystal and it was set in the bottom of crucible. All the processes mentioned above were performed in a glove box filled with Ar gas. The removable chamber was taken out from the glove box after the hotzone set up. The grown crystal was taken out from the chamber in the glove box.

In the result, the 2 inch Eu:SrI₂ bulk crystal without visible crack was obtained. It had high transparency and there was no visible inclusion in the crystal. The crystal was cut and polished in the glove box and was sealed into the aluminum container with an optical window. The detail of crystal growth and scintillation properties of 2 inch Eu:SrI₂ bulk crystal will also be reported.

In an effort to reduce the cost of single crystal production of metal halide based scintillator materials, we have experimented with the simultaneous melt growth of large diameter boules (≈6") using a modified vertical Bridgman furnace developed in our laboratory. Borrowing from technology used in the production of monocrystalline oxide based piezoelectric and scintillation materials, we adopted the multi-crucible furnace design to the production of bulk metal halide crystals with cylindrical form. We demonstrate the applicability of the multi-ampoule furnace design to this material class by presenting the results from simultaneous growth of 5 cylindrical boules at Ø22mm using a newly developed Multi-Ampoule-Growth-Station (MAGS). The spectroscopic performance as well as the macro-scale defect structure is compared between the 5 boules grown in parallel using the nonconventional furnace design. CsCaI₃:Eu, a promising scintillator material, was synthesized and grown into crystal ingots approximately Ø22mm x 50mm L in fused silica ampoules. A growth rate of 0.25mm/HR and cooling rate of ≈4°C/HR was successful in producing crystal boules with a high degree of translucency with minimal cracking. Evidence of twinning in all the boules suggests a source for the reduction in transparency. A vertical thermal gradient of 18°C/cm in the solidification zone was maintained and variances of ±3°C were measured for each ampoule bay by embedded thermocouples surrounding each growing boule. A special bent capillary geometry was used for promoting a randomly oriented self-seed which resulted in some boules having a monocrystalline grain structure while others exhibited evidence of wall nucleated grains. Spectroscopic performance was measured for polished slabs of Ø0.25 - 0.5in3 in volume taken from each of the 5 boules. The measured energy resolution of the 662 KeV photopeak from a 137Cs source ranged between 6-9% (FWHM/Centroid) across all boules. Poorer performance was correlated to the boules with wall-nucleated grain structures. The present results are a significant improvement over previous performance of CsCaI₃:Eu with prior reports of 8-16% energy resolution at 662 KeV. The demonstrated synthesis method may provide an economical advantage for bulk crystal growth of many metal halide compositions.
Many halide crystals have excellent scintillator properties making them useful for radiation detector applications. Some of the newer, more efficient crystals, however, are very expensive and therefore deployment is financially prohibitive. The EFG method permits the growth of shaped crystals at higher growth rates than many other crystal growth methods. This increases production throughput and reduces machining costs. The method involves pulling crystals from shaped dies placed on or in the melt surface. The die not only shapes the crystal cross-section but also provides steeper thermal gradients at the growth interface.

The EFG growth of SrI₂, one of the most important new scintillator compounds, will be discussed. SrI₂ is deliquescent and requires special handling at all stages of growth, sample preparation and crystal characterization. In these experiments floating graphite, quartz and AlN dies were used. Both round and square cross-section crystals of both materials were grown at rates up to 20 mm/hr and 8 cm long. SrI₂ crystals grown from graphite dies contained scattering centers giving the crystals a milky appearance. The growth system and parameters will be discussed along with examples of the large single crystals produced, defects and thermal modeling studies.
The importance of gamma ray spectroscopy in the age of nonproliferation can hardly be overstated. While the industrial use of gamma ray spectroscopy is constantly changing, what remains is the need for crystals with good energy resolution and low non-proportionality. Devoid of native radioactive isotopes, europium doped strontium iodide is prime for commercialization. In this report, we use codoping to optimize crystal toughness and scintillation properties through the substitution effect of univalent and divalent ions substituted at the strontium site of a strontium iodide doped with 2.5 mol% europium matrix.

The material, strontium iodide (99.999% purity beads) doped with 2.5 mol% europium iodide (99.999% purity beads), was synthesized using quick Bridgman then partitioned into 10 g charges for the use of the different codopants. Using a custom fabricated steel cartridge machined in the shape of a revolver cylinder, five ingots were grown simultaneously in one Bridgman run. Considering the long growth time (3-4 weeks), the use of the cartridge allowed the fast growth and test of multiple crystals, thereby allowing for higher throughput. The steel cartridge allows the growth of five ingots simultaneously in one Bridgman run.

Figure 2 showed a magnesium codoped sample, ICP-MS was performed on the crystal and less than 10 ppm of Mg was found on the first to freeze portion. Magnesium iodide is extremely hygroscopic and we assume it is acting as a moisture getter accumulating excess moisture from the SrI$_2$ to the last to freeze portion leaving a crack free crystal. This is particularly impressive as the crystal was grown in a 10 mm ampoule which has comparatively worst heat extraction than a typical larger diameter ampoule in the growth furnace. We have obtained preliminary gamma-excited scintillation measurements and are presented in Table 1. The best energy resolution of 2.9%, and crystal quality of the grown boules was obtained for the magnesium codopant. The increased trapping leads to improved predicted performance from a decreased amount of Birks Quenching (Figure 4). It should also be noted that ions are not necessarily homogeneously incorporated within the matrix so it may also serve as a moisture getter.

Table 1: Codoped samples

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Resolution at 662 keV (%)</th>
<th>Decay Time (ns)</th>
<th>Light Yield (x NaI)</th>
<th>Ionic Radius Normalized to Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI$_2$:Eu$^{2+}$ (2.5 mol%)</td>
<td>3.4</td>
<td>1000</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Ca$^{2+}$ (2.5/1 mol %)</td>
<td>4.2</td>
<td>854</td>
<td>2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Mg$^{2+}$ (2.5/1 mol %)</td>
<td>2.9</td>
<td>1020</td>
<td>2.5</td>
<td>0.7</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/K$^{+}$ (2.5/1 mol %)</td>
<td>4.1</td>
<td>708</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Na$^{+}$ (2.5/1 mol %)</td>
<td>3.1</td>
<td>845</td>
<td>2.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>
A new, high light yield metal halide scintillator KCaI$_3$:Eu with 75,000 ±5,000 ph/MeV has been successfully grown using the Vertical Bridgman Technique (VBT) at Ø 17mm and 30mm in length. The compound belongs to the perovskite type orthorhombic crystal family with ABX$_3$ formula and exhibits favorable behavior for melt growth of bulk crystals. Special attention to the self-seeding process ensures a randomly oriented single crystal can be grown without a pre-existing seed. Differential scanning calorimetry indicates a singular endo/exothermal peak of fusion (T$_m$=524°C) with no evidence of solid-solid phase transformations. While requiring no significant preprocessing of the as received raw material, we demonstrate that yellow tinted, yet water clear crystals of $\approx 3.5$cm$^3$ can be grown using conventional VBT in fused silica ampoules.

Under irradiation from a 137Cs source, small specimens of a few mm$^3$ produce energy resolutions (FWHM/Centroid) of $<\%$ at 662 KeV. This result is comparable to that of the highest energy resolution achievable in scintillators such as LaBr$_3$:Ce and SrI$_2$:Eu ($<3\%$). A larger specimen measuring Ø17mm x 17mm produced 4.4% energy resolution at the same energy. Proportionality of the scintillation response to energies across the 14KeV-835KeV range is better than 96% indicating potential for further improvement to the energy resolution as growth processes are optimized. Scintillation lifetimes for small specimens are typically under 1µs, especially good for Eu activation. While still early in development, this material may have significant potential for use in security applications requiring single crystal scintillators which can be produced in large volumes at low cost, possessing higher energy resolution than commonly used thallium doped sodium iodide (NaI:Tl).
The exceptional thermal stability, tunable porosity, unique shape-selectivity, and high acidity of zeolites contribute to their frequent use as catalysts and adsorbents. The inability to a priori control crystal growth, however, often yields materials with undesirable physicochemical properties. Approaches capable of selectively tailoring zeolite size, morphology, and/or crystal structure can lead to dramatic improvements in their performance. Given the application of zeolites in areas of biomass and methane conversion, CO₂ sequestration, and selective separations, there exists a need to expand the fundamental understanding of zeolite growth as well as design synthetic routes to optimize their properties. In this talk, we will discuss a new advancement in atomic force microscopy (AFM) that has enabled us to image zeolite surface growth in situ under realistic synthesis conditions (i.e., high temperature and long duration). AFM offers unparalleled insight of dynamic processes governing zeolite growth at near-molecular resolution. We used in situ AFM to characterize zeolite surface growth over the course of 10-30 hours of continuous scanning. A systematic study of silicalite-1 revealed that growth occurs by two concurrent mechanisms: a classical route (i.e., molecule addition) and a non-classical pathway defined by the addition and subsequent rearrangement of amorphous precursor particles. We will discuss these findings and place their significance within the broader context of other zeolite crystal structures that grow by a variety of different pathways.


A colloidal crystal is regarded as a promising tool to investigate diverse basic physical phenomena. We have applied this colloidal crystal to impurity partitioning in the melt growth. For the growth of single colloidal crystals, we have confirmed that impurity partitioning is similar to that of normal crystal growth, in which BPS model and Thurmond and Struthers (T&S) were applied. Here, in-situ observation has been carried out on the growth of colloidal polycrystalline to reveal detailed partitioning behavior. Polystyrene with 500 nm in diameter was used for host particles of colloidal crystals, and different sized was doped as impurity. Convective assembly method is employed for growing crystals. Colloidal crystals are grown in a cell, in which colloidal solution is sandwiched with cover slips. Since thickness of the solution is ~micron, two to three layers of colloidal crystals grow. Polycrystalline colloidal crystals were grown in the cell. Though all of grain has fcc structure, two types of grains were observed. Grains oriented along <111> or <100> direction to wall of cover slips were compared. Equilibrium partition coefficient, k, of <111> was found to have larger value than that of <100>. We have employed a T&S theory to discuss the difference of k, T&S model shows k, as k = exp((dG−dH)/RT). Here, dG is free energy difference between the solid and liquid phases of an impurity at the transition temperature, T, dH is the excess enthalpy that is caused by incorporation of the impurity into the host material, and R is a gas constant. For the single colloidal crystals, difference of k, was well explained if volume fraction instead of temperature is used to evaluate dG (Nozawa et al., 2013), because it is driving force for colloidal crystallization. The same discussion was applied here.

Volume fraction of <100> oriented grain is smaller than that of <111> when their layer is less than three. This difference gives different dG for <111> and <100> oriented grains, leading to different k. During growth of colloidal polycrystalline, impurity segregation at grain boundary (GB) was observed. The impurity concentration in GB, C_{imp}, was found to increase with increasing growth rate and angle between two grains separated by GB. From the in-situ observation, it has been revealed that most of impurities incorporated into GB are supplied from the segregated impurities at GB.

When continuum methods are used to model crystal growth, typically an anisotropic surface energy function is selected. These functions describe surface free energy on a facet depending on its orientation. However, it may be that not all such functions should be admissible when modelling real materials. We examine a simple bond-counting model using Kinetic Monte Carlo methods, to determine the relationship between a crystal’s lattice structure, its inherent surface free energy, and its growth shape. Comparing the two types of models, we demonstrate that not all growth shapes seen in continuum models are easily recreated in bond-counting models. Specifically, we show that a 12-armed dendrite as modeled in Haxhimali et al. is not a possible growth shape using a bond-counting model on an FCC lattice considering nearest- and next-nearest-neighbor bonds.
The effects of axial magnetic field on the morphology and growth of Ni48Mn24Ga22 during directional solidification were investigated. The axial magnetic field has a remarkable influence on the directional solidification structure of Ni-Mn-Ga alloys. After applying the axial magnetic field, the solid-liquid interface becomes smoother and the dendrite length turns shorter with the increase of the axial magnetic field intensity. When the axial magnetic field intensity reaches 2T, some dendrites are twisted off and the original monocrystalline specimen becomes polycrystalline specimen. These are caused by the thermoelectric magnetic convection and the thermoelectric magnetic force. When the axial magnetic field intensity is large enough, the thermoelectric magnetic force can twist off the dendrite. The crystal orientation and texture of Ni-Mn-Ga alloys under the directional solidification are experimentally studied by electron backscatter diffraction (EBSD). The crystal-selected phenomenon of Ni-Mn-Ga alloys under the directional solidification becomes obvious gradually with the increasing of the growth rate, and the crystal orientation is just right for the preferential growth orientation (001) of the original austenitic Ni-Mn-Ga alloys. The transverse magnetic field (B<1T) has a weak influence on the crystal orientation under the directional solidification, which is the same as the effect of non-magnetic field. Nevertheless, when the axial magnetic field is applied during the directional solidification, the thermoelectric magnetic force (TEMF) becomes large enough to twist off the dendrites. As a consequence, the specimen becomes polycrystalline specimen, which crystal orientation is consistent along the longitude and disordered along the radial direction. In addition, the disordered martensitic blocks tend to grow consistently along the direction of the axial magnetic field after the application of the axial magnetic field.
GaInP is important to use in wide band-gap semiconductors for applications in high-power or high-frequency devices [1]. There is high possibility that GaIn replace the conventional III-V complex materials [2]. However, dislocation is the serious problem for degradation of performance for GaIn.

Fig. 1 Distributions of dislocation density at room temperature for GaN ingots grown by (a) sapphire substrate and fast cooling rate, (b) sapphire substrate and slow cooling rate, (c) GaN substrate and fast cooling rate and (d) GaN substrate and slow cooling rate. To improve the performance of GaN devices, it is necessary to reduce the dislocation density. It has been reported that the multiplication of grown-in (or threading) dislocations mainly caused by the motion on prismatic slip planes [3]. We extend the Haesen-Alexander-Sumino model to describe the grown-in dislocation multiplication by prismatic slip in GaN single crystals [3]. In this study, we take into account dislocation density caused by thermal stress, not caused by lattice mismatch. And we investigate the effect of substrate and cooling rate on dislocation density by numerical analysis.

We used two different substrates, sapphire and GaN based on the GaN LPE growth to investigate the effect of difference in thermal conductivity and coefficient of thermal expansion between substrate and GaN grown crystal on dislocation density. And we also investigate the effect of cooling rate during the cooling process on dislocation density. Fig. 1 shows the distributions of dislocation density at room temperature for GaN ingots using different substrates and cooling rates. The result shows that dislocation density for GaN substrate is lower than that for sapphire substrate because difference in thermal conductivity and coefficient of thermal expansion between substrate and GaN grown crystal is small. And in this LPE furnace configuration, fast cooling rate could reduce the grown-in dislocation density. This result causes that temperature difference at radial direction decreased faster in the high temperature region by fast cooling rate. The effect of cooling rate on dislocation density is larger than that of substrate. Therefore, it is important to reduce the dislocation density to take into account for cooling rate during the cooling process.

REFERENCES
GaN seeds, F-S HVPE-GaN can be successfully used as a seed for further HVPE-GaN growth. It is feasible to multiply the ammonothermally grown GaN by the HVPE technology. The F-S HVPE-GaN crystals can also be used as seeds for the ammonothermal, as well as the High Nitrogen Pressure Solution (HNPS) growth. In this paper the state of the art of HVPE-GaN growth on 1-, 1.5- and 2-inch Am-GaN seeds will be demonstrated. Particular attention will be paid to the growth rate and its influence on the structural quality and purity of the HVPE-GaN layers. For 1-inch Am-GaN seed a strain generated in the new-grown HVPE material as well as in the seed will be analyzed. It will be shown that this strain appears due to the lattice mismatch between the Am-GaN seed and the HVPE-GaN layer. Additionally, the strain can be derived from HVPE-GaN wings crystallized on the edges of the HVPE-GaN grown in the c direction. The wings grow in non-polar and semi-polar directions. Due to a high free carrier concentration, the lattice constants of the wings are much larger than the lattice constants of the HVPE-GaN layer. It will be, however, demonstrated that a relatively thin, 300-mm-thick, 1-inch Am-GaN substrate is easily elastically bent. Therefore the strain generated in the HVPE-GaN layer can be compensated. It will be also shown that the negative influence of HVPE-GaN wings can be reduced for larger in diameter (1.5- and 2-inch) seeds.

New directions in the development of the HVPE-GaN growth will be presented. The main goal for today is to develop a method of doping by donors (silicon and germanium) and acceptors (carbon and iron). It seems that due to the high purity of the HVPE-GaN, the free carriers can be compensated at a very low level of doping. Thus, high-quality HVPE-GaN with a high resistivity should easily be obtained. On the other hand, high-quality HVPE-GaN with the free carrier concentration of the order of 5x10^18 cm^-3 should also be crystallized.
Second Symposium on 2D Electronic Materials (Joint ACCGE/OMVPE)

10:30 AM - 12:00 PM

**MATERIALS SCIENCE WITH 2D ATOMIC LAYER BUILDING BLOCKS**

**Invited**

**Pulickel M. Ajayan**
Rice University, Houston, TX

There has been tremendous interest in recent years to study isolated 2D atomic layers which form the building blocks of many bulk layered materials. This interest was initiated by the spectacular discovery of graphene which has been demonstrated to have a unique set of properties. This talk will focus on the materials science of graphene and the emerging field of 2D atomic layers beyond graphene. Our group has been working on 2D materials systems such as graphene, graphene oxide, boron-nitrogen-carbon containing materials and several compositions of transition metal dichalcogenides. Several aspects that include synthesis, characterization and device fabrication of these systems will be discussed with the objective of building all 2D functional structures for future technologies. There are several challenges in growing and fabricating devices with 2D atomic layers, including scalability, uniformity, defects, stability, stacking, contacts etc. and the talk will discuss these issues and the progress made in addressing these. The concept of nanoscale engineering and the goal of creating new artificially stacked van der Waals solids will be discussed through a number of examples including graphene and other 2D layer compositions.

**BUILDING HETEROSTRUCTURES AND DOPING WITH METAL CHALCOGENIDES: TUNABLE PROPERTIES AND POSSIBLE APPLICATIONS**

**Invited**

**Nestor Perea**
The Pennsylvania State University, University Park, PA

This talk will discuss the synthesis of large-area, high-quality monolayers of nitrogen-, boron- and silicon-doped graphene sheets on Cu foils using ambient-pressure chemical vapor deposition (AP-CVD). Scanning tunneling microscopy (STM) and spectroscopy (STS) reveal that the defects in the doped graphene samples arrange in different geometrical configurations exhibiting different electronic and magnetic properties. Interestingly, these doped layers could be used as efficient molecular sensors and electronic devices. In addition, the synthesis of hybrid carbon materials consisting of sandwich layers of graphene layers and carbon nanotubes by a self-assembly route will be discussed. These films are energetically stable and could well find important applications as field emission sources, catalytic supports, gas adsorption materials and super capacitors.

Beyond graphene, the synthesis of other 2-Dimensional materials will be described. In particular, we will discuss the synthesis of WS2 and MoS2 triangular monolayers, as well as large area films using a high temperature sulfurization of WOX clusters deposited on insulating substrates. We will show that depending on the substrate and the sizes of the oxide clusters, various morphologies of layered dichalcogenides could be obtained. In addition, photocurrent measurements on these materials will be presented. Our results indicate that the electrical response strongly depends on the laser photon energy. The excellent response observed to detect different photon wavelengths in MoS2, WS2 and WSe2 materials, suggest these materials could be used in the fabrication of novel ultrafast photo sensors. We will also show that these techniques are able to produce in-plane heterojunctions with sharp interfaces of MoS2 and WS2. The material exhibits novel excitonic effects that will be discussed.

From the theoretical stand point, we have found using first principles calculations, that by alternating individual layers of different metal chalcogenides (e.g. MoS2, WS2, WSe2 and MoSe2) with particular stackings, it is possible to generate direct band gap bilayers ranging from 0.79 eV to 1.157 eV. Interestingly, in this direct band gap, electrons and holes are physically separated and localized in different layers. We demonstrate that it is possible to alternate different chalcogenide layers with graphene and hBN with unprecedented optical and physico-chemical properties.

**ULTRA LOW NOISE GRAPHENE BASED ELECTRONICS**

**Invited**

**Alton Horsfall**
Newcastle University, Newcastle, United Kingdom

The experimental performance of graphene does not match theoretical predictions, due in part to the methods of material synthesis and subsequent device fabrication processes, which introduce unintentional defects into the system. For epitaxial graphene films grown on the silicon face of SiC, interactions between the graphene and the underlying silicon carbide gives rise to transfer doping and a source of carrier scattering. In addition, the interaction of the graphene film with a dielectric layer for the realization of a field effect transistor structure (GFET) may result in further deterioration of the device performance. Functionalisation of the graphene surface prior to deposition of the dielectric enables a more conformal dielectric to be deposited by ALD, as well as reducing the contact resistance of the metal contacts.

In addition to conventional parametric testing, analysis of the low frequency noise has been used to determine the origin of defects in GFET structures. Whilst results in the literature report that the gate electrostatic (VG) modulated noise is described by the Hooge model, our results show that the normalized noise power spectral density (SII/I2) is proportional to the square of channel resistance.
This is similar to results for silicon based transistors, where the noise is described by the interaction of the carrier with the SiO2 interface. In contrast, the intrinsic noise characteristics (without gate bias) illustrate an inverse relation with the Hall effect mobility and weakly dependent on the RSH. This suggests a two distinctive noise generation sources that dominates the intrinsic and gate modulated characteristics.

Noise measurements have also been used to identify the origin of chemical interactions with a graphene surface, when used as a chemoresistive sensor for polar solvents. Measurements show the existence of a generation/recombination mechanism for frequencies below 10Hz, which can be interpreted as the interaction of carriers with trapping centres activated by the solvent incident on the surface.

The presentation will describe the findings and how these are utilized in the quest to produce ultra low noise electronic devices based on epitaxial graphene.
Monday, August 3, 2015
1:30 PM - 3:00 PM

Correlated Electron Crystals 2

Location: Lake/Canyon
Session Chair(s): Athena Safa-Seattle, John E. Greedan

1:30 PM - 2:00 PM

STRONG COMPETITION BETWEEN ORBITAL ORDERING AND ITINERANCY IN A FRUSTRATED SPINEL VANADATE
Invited
haidong zhao
University of Tennessee, Knoxville, TN

The transformation from itinerant to localized spins in geometrically frustrated systems can create exotic phases by modifying the relationship between the spin, orbital, and lattice degrees of freedom. Although the competing effects of localized and itinerant behavior on magnetic frustration have been rather extensively investigated on triangular and pyrochlore lattices, they have rarely been explored for the frustrated spinel AB2O4. Spinel vanadates exhibit additional intriguing characteristics due to the orbital ordering (OO) of the partially filled (3d2) B sites. In this talk, we first introduce the single crystal growth of the spinels such as AV2O4 and ACr2O4. Then we discuss the complex magnetic phase diagrams of AV2O4 resulted from the strong competition between orbital ordering and itinerancy on the frustrated V3+-pyrochlore sublattice.

2:00 PM - 2:15 PM

CRYSTAL GROWTH OF VANADATES IN DIFFERENT OXIDATION STATES
Casey A. Marjerrison1, Hanna A. Dąbkowska2, Matthieu Bugnet1, Bruce D. Gaulin2, Antoni Dąbkowski2
1Department of Physics and Astronomy, McMaster University, Hamilton, ON, Canada, 2BIMR, McMaster University, Hamilton, ON, Canada

Optical floating zone (OFZ) proved itself many times as an useful technique to grow crystals of complicated new oxides with interesting physical properties [1]. Those include, but are not limited to, giant permittivity perovskite CaCu3Ti4O12 [2] and incongruently melting high temperature superconductors (ex Bi2223) [3]. This technique allows also to obtain good quality, relatively large crystals, where transition metal exists in different oxidation states (example of mixed valence crystals - Mn3O4 [5] or MgTi5O9). Another case is of crystals where the same element can be found in different oxidation state - and in different crystallographic structure. In the RE-V-O (RE=Rare Earth) system atomic ratio of RE:V=1:1 gives as series of compounds where, respectively, V+3, V+4 and V+5 can be observed. Recently, large, good quality single crystals of LVO4, LuVO3 and Lu2V2O7 were grown by the OFZ in our laboratory. Ceramics preparation and a comparison of crystal growth conditions are reported. Different vanadium oxidation states were obtained using different growth atmospheres and pressures. Obtained crystals were characterized by magnetic measurements, x-ray and electron diffraction techniques. Due to the fact that OFZ is a crucibleless method and due to relatively simple atmosphere and pressure control, the OFZ is an ideal technique for this type of material research.


2:30 PM - 3:00 PM

BOND DIRECTIONAL ANISOTROPY AND THE APPROACH TO A QUANTUM SPIN LIQUID IN A HONEYCOMB IRIDATE
Invited
John F. Mitchell1, SaeWan Chun1, Jung-Ho Kim1, Jong-woo Kim1, Thomas Gog1, Yong Choi1, Konstantinos Stoumpos1, Christos Malliakas1, Hong Zheng2, Jiri Chaloupka2, Yogesh Singh2, Kavita Mehawat2, Ali Al Zein3, Michael Moretti4, Michael Krisch4, Giniyat Khaliullin5, George Jackeli2, Bum Joon Kim4
1Argonne National Laboratory, Argonne, IL; 2Central European Institute for Technology, Brno, Czech Republic; 3Indian Institute of Science Education and Research, Mohali, India; 4ESRF, Grenoble, France; 5Max Planck Institute, Stuttgart, Germany

Traditional approaches to stabilizing quantum spin liquids (QSL) have heavily relied on the geometrical frustration of antiferromagnetically coupled spins on lattices with triangu lar motifs such as pyrochlore and kagome structures. An alternative route is to exploit anisotropic interactions, which are intrinsically bond-directed and hence compete with one another. A prime example is the Kitaev model, which has a QSL as the exact solution but has yet to find a material realization. Here, we show that such bond-directional interactions govern the spin dynamics of the 5d transition-metal oxide Na2IrO3 and lead to a strong magnetic frustration in a honeycomb lattice. Diffuse magnetic x-ray scattering reveals that spin-rotational symmetry is strongly broken even above the magnetic ordering temperature, with the three spin components exhibiting nano-scale correlations along three different crystallographic directions. This spin-component separation in real space provides direct evidence for dominant bond-directional interactions in Na2IrO3 and establishes a new route toward frustrated magnetism.
DEFECT ENGINEERING AND GROWTH OF Sb:BiI3 FOR ENHANCED NUCLEAR RADIATION SEMICONDUCTOR DETECTORS

Invited
Juan Claudio Nino1, Paul Johns1, Kelly Jordan2, Mary Bliss1, James Baciak1
1University of Florida, Gainesville, FL, 2Pacific Northwest National Laboratory, Richland, WA

BiI3 is a wide band-gap compound semiconductor with a high effective atomic number that has been anticipated to exhibit higher detection efficiency than other compound semiconductors such as Hgl2, PbI2, and CdZnTe. This makes BiI3 of particular interest for moderate and high energy gamma-ray detection applications. However, until recently the low resistivity of BiI3 resulted in high leakage currents and degradation of the electrical properties thus limiting the detecting performance of the detectors. Here we show that the main reason for the low resistivity in BiI3 is due to the high volatility of iodine and the high concentration of intrinsic Schottky defects. Furthermore, we will discuss novel defect engineering strategies that successfully mitigate the obstacles associated with iodine vacancies in the material. Specifically, the electrical properties and radiation response of both undoped and Sb-doped BiI3 (Sb:BiI3) single crystals grown via the vertical Bridgman growth technique will be presented. We will show that Sb incorporation as a dopant effectively limits the formation of iodine vacancies and also strengthens the naturally soft layer compound. Moreover, in this talk we will present the results of an investigation performed on the microstructure of Sb:BiI3 that led to the discovery of void inclusions within the bulk of Bridgman grown crystals. We will show that employing a superheating gradient step during the crystal growth process effectively reduces the presence of voids, resulting in a significant improvement in the crystal quality. These combined enhancements (defect engineering and growth profile optimization), has yielded superheated Sb:BiI3 crystals with improved electronic properties, enhanced structural integrity, and spectral sensitivity which surpasses normally grown crystals. Finally, we will demonstrate and discuss the effect of these growth enhancements on the quality of the gamma-ray spectra collected using BiI3-based detectors.
Single crystals of lead based semiconductors were grown for potential cost-effective X-ray/γ-ray detection applications. Large crystal ingots of the target materials up to 30mm in length and 10mm in diameter were grown by a vertical Bridgman method. Cutting and polishing procedures have been optimized to produce size-appropriate sample wafers for physical, optical, photo-transport property studies as well as γ-ray detector testing. These materials exhibit large optical bandgaps ~ 1.9eV and electrical resistivity in the range of 1x10¹⁰Ωcm, which are desirable properties for hard radiation detection. In addition, these compounds showed congruent melting behaviors as well as robust chemical/physical properties that promise low cost bulk production and detector development. Single crystal samples of these lead based semiconductors displayed significant photo-conductivity responses when illuminated with 40 keV Ag X-ray. When tested with ⁵⁷Co γ-ray radiation, many samples showed spectroscopic responses and a few of them were able to generate partially resolved ⁵⁷Co spectra.

2:45 PM - 3:00 PM
GROWTH AND CHARACTERIZATION OF UO2 AND NOVEL URANIUM CRYSTALS FROM HYDROTHERMAL SOLUTIONS
J. Matthew Mann¹, Eric Hunt¹, Glenn Peterson¹, Tony Kelly¹, David Turner¹, James Petrosky²
¹Air Force Research Laboratory, Wright-Patterson AFB, OH, ²Air Force Institute of Technology, Wright-Patterson AFB, OH, ³Oak Ridge Institute for Science and Education, Oak Ridge, TN

Recently, there is a renewed interest in developing small, efficient, gamma blind, fission based neutron detectors and radiation hardened devices by design from UO₂ single crystals. However, UO₂ crystal growth has proven difficult due to the high melting point (2878°C), which precludes the use of traditional melt growth techniques like Czochralski. Although UO₂ crystalization has been realized by exotic melt growth techniques such as arc fusion, cold crucible, and solar furnace, the crystals are of poor quality due to thermal strain and oxygen non-stoichiometry due to the rapid oxidation of UO₂ to hyperstoichiometric UO₂⁺, under most growth conditions. Lower temperature techniques like flux growth have also been successful in growing UO₂ from a Na₂B₂O₅ flux at ~1100°C. Unfortunately, boron solvent inclusions in the crystal serve as unintentional dopants which affect the conductivity. Hydrothermal growth is a relatively low temperature technique, which has demonstrated synthesis of high quality, high purity crystals for several refractory oxides. Therefore, a hydrothermal growth study was conducted to determine the solvating conditions and phase stability of UO₂ in a variety of mineralizer solutions. Growth of spontaneously nucleated UO₂ crystals up to 250[Unsupported Character - Symbol Font &#61549;]m was achieved in several alkali hydroxide and fluoride mineralizers over a temperature range of 600-650°C. Identification and measurement of the UO₂ phase and stoichiometry was determined by single crystal X-ray diffraction. During the study, six novel uranium species were also isolated. In particular the crystal structure and electronic properties of the novel RbUPO₄ structure was examined in detail by X-ray diffraction, inverse photoemission spectroscopy, ultraviolet photoemission spectroscopy, and X-ray photoemission spectroscopy. These results will be presented along with the growth morphology of the UO₂ crystals.

3:00 PM - 3:15 PM
HYDROTHERMAL GROWTH AND CHARACTERIZATION OF BULK UO2 CRYSTALS
Eric Hunt¹, J. Matthew Mann¹, Christopher Young¹, David Turner¹, James Petrosky²
¹Air Force Research Laboratory, Wright-Patterson AFB, OH, ²Air Force Institute of Technology, Wright-Patterson AFB, OH, ³Oak Ridge Institute for Science and Education, Oak Ridge, TN

Single crystals of UO₂, with elevated isotopic ratios of ²³⁵U to ²³⁸U, are being investigated for gamma blind neutron detectors. The energy-dependent neutron fission cross sections of ²³⁵U and ²³⁸U provide both a thermal and fast neutron sensitivity. The ionized fragments from a fission event would generate electron-hole pairs in the UO₂ crystal lattice to be directly registered without the need for a secondary detector. A UO₂ lattice with sufficient conductivity is required for this application. Recently, UO₂ with p-type conductivity has been demonstrated by ion implantation of dopants into a thin surface layer of crystals grown by the arc fusion method. The 6-10 micron migration of the decay products rarely terminates in the 0.21 micron thick surface layer, which limits the efficacy of these samples. A bulk, well-oriented UO₂ crystal with homogeneous doping is the optimal arrangement, but a method to synthesize high quality single crystals has yet to be developed. This study demonstrates for the first time bulk growth of UO₂ by the hydrothermal synthesis technique. UO₂ seed crystals of substantial size (> 3 x 3 x 3 mm) were spontaneously nucleated (SN) from a CsF mineralizer solution for bulk transport growth reactions. The process of generating the SN seeds and the subsequent growth will be presented. Additionally, UO₂ growth on non-native substrates of CaF₂ was achieved due to a low lattice mismatch of 0.102%. Structural and electronic characterization of the UO₂ crystals was investigated by X-ray diffraction, X-ray fluorescence spectroscopy, X-ray photoemission spectroscopy, and ultraviolet photoemission spectroscopy.
PROTEIN CLUSTERS AND CRYSTALS AT BIRTH
Invited
Dominique Maes, Maria A. Vorontsova, Tiziano Sanvito, Marco AC Potenza, Marzio Giglio, Mike Sleutel, Peter G. Vekilov
1 Vrije Universiteit Brussel, Brussels, Belgium, 2 University of Houston, Houston, TX, 3 Universita di Milano, Milano, Italy

The protein dense liquid clusters are regions of high protein concentration that have been observed in solutions of several proteins. The typical cluster size varies from several tens to several hundreds of nanometers and their volume fraction remains below 10^-3 of the solution. According to the two-step mechanism of nucleation, the protein-rich clusters serve as locations and precursors to the nucleation of protein crystals. While the two-step mechanism explained several unusual features of protein crystal nucleation kinetics, a direct observation of its validity for protein crystals has been missing. We will discuss two independent observations of crystal nucleation with the protein lysozyme and glucose isomerase. First, we characterize simultaneously the evolutions of the protein-rich clusters and nucleating crystals by, respectively, dynamic light scattering (DLS) and confocal depolarized dynamic light scattering (cDDLS). Second, depolarized oblique illumination dark-field microscopy reveals the evolution from liquid clusters without crystals, to newly-nucleated crystals contained in the clusters, to grown crystals freely diffusing in the solution. Collectively, our observations indicate that the protein-rich clusters in lysozyme and glucose isomerase solutions are locations for crystal nucleation.

SELECTIVE CRYSTALLIZATION OF ACETAMINOPHEN POLYMORPH WITH HIGH SOLUBILITY
Yoichiro Mori, Mihoko Maruyama, Yoshinori Takahashi, Hiroshi Yoshikawa, Shino Okada, Hiroaki Adachi, Shigeru Sugiyama, Kazufumi Takano, Satoshi Murakami, Hiroyoshi Matsumura, Tsuyoshi Inoue, Masashi Yoshimura, Yusuke Mori
1 Osaka University, Japan, 2 Osaka University and SOSHO Inc., Japan, 3 Osaka University and Saitama University, Japan, 4 SOSHO Inc., Japan, 5 Kyoto Prefectural University and SOSHO Inc., Japan, 6 Tokyo Institute of Technology and SOSHO Inc., Japan

Acetaminophen is one of the most widely used antipyretic and analgesic drugs in the world. It is known that acetaminophen has three polymorphs: form I, II and III. Form I (stable phase) which has the lowest solubility of three polymorphs is used in commercial formulations. Form II and III show low stability (easily transform to stable phase) and the method for selective crystallization of form II and III is not well established. In this study, for the purpose of crystallizing form III (the most unstable phase), we investigated effects of additives on acetaminophen polymorphism.

Aqueous acetaminophen solution (40 mg/ml) was prepared by dissolving acetaminophen in ultrapure water at 70 °C. After filtration, the solution was dispensed in 0.8 ml aliquots into 1-ml glass vials. These samples were then cooled to 0 °C and maintained at that temperature (supersaturation $\sigma_I = 4.9$). Additive A (one of the polymers) was previously added to glass vials prior to dispensing (8 samples). For the purpose of comparison, we also prepared additive-free samples (4 samples). We investigated the crystallization probability and measured the solubility of crystals obtained by addition of the additive. In the case of the additive-free system, spontaneous crystallization did not occur for a month after the solution temperature reached 0 °C. On the other hand, when additive was added, we confirmed the crystallization of acetaminophen in all 8 samples within 2 days after the solution temperature reached 0 °C. The solubility of these crystals at 20 °C was about 1.8 times higher than that of form I, and 1.5 times higher than that of form II. These results indicate that there is a possibility that the obtained crystals is form III, hydrate or another new polymorph. We intend to investigate the stability and attempt the structural analysis of the obtained crystals in the future.
Bi incorporation into GaAs results in a large bandgap energy reduction (60-80 meV per mole percent Bi in GaAs$_{1-x}$Bi$_x$). The associated increase in spin-orbit splitting leads to a decreased Auger recombination process allowing for a reduction in fundamental carrier loss processes. These promising optoelectronic properties have led to the study of the growth of GaAs$_{1-x}$Bi$_x$ in recent years.

The challenge of Metal-Organic Vapor Phase Epitaxy (MOVPE) growth of GaAs$_{1-x}$Bi$_x$ lies in that, as Bi is highly immiscible in GaAs, the Bi surface segregation is expected. The surface transport and incorporation rate of both Bi and Ga can be dependent on the specific atomic surface structure and are expected to be crystal-orientation sensitive. In this work, through the growth of GaAs$_{1-x}$Bi$_x$ by MOVPE on patterned GaAs substrates containing disc-shaped and stripe-shaped mesas, the anisotropic nature of the surface transport and incorporation were investigated.

The growths on disc-shaped mesas evolve from a circular to an oblong shape as growth proceeds, with being the fastest GaAs$_{1-x}$Bi$_x$ lateral growth direction, until Bi droplets form at the edge. Increases in the Bi precursor gas phase mole fraction results in lower lateral growth rate. On samples possessing Bi droplets, the highest droplet density is located at the mesa edges, with Bi accumulating more strongly at mesa edges. Additionally, the Bi droplets also serve as sites for GaAs$_{1-x}$Bi$_x$ micro-sized wire growth, formed through the vapor-liquid-solid (VLS) mechanism. Reciprocal space mappings (RSMs) for samples free of Bi droplets show only one peak for the GaAs$_{1-x}$Bi$_x$ with x=0.019, while RSMs from samples with Bi droplets show an extra Bragg peak associated with a higher Bi concentration x=0.029, which may be associated with the GaAs$_{1-x}$Bi$_x$, micro-wire growth either through changes in composition within the micro-wire or over a surrounding area.

The observed anisotropic lateral growth rate and Bi accumulation behavior may indicate either a preferred Ga/Bi surface diffusion along [-110] direction, and/or a higher Ga/Bi diffusion energy barrier on the [-110] step edges. By assuming the diffusion length to be at least the radius of the mesa and considering the surface area for accumulating Ga/Bi, the minimum diffusion coefficient of Ga and Bi on (001) surface is estimated to be 5.4x10$^{-8}$ cm$^2$/s and 2.5x10$^{-9}$ cm$^2$/s, respectively. These growth studies on patterned substrates allow some of these important surface site-specific processes to be probed and understood.

**Fig. 1** Anisotropic lateral growth
Fig. 2 Bi accumulation and VLS growth under Bi droplets
(a) Plan-view  (b) Plan-view  (c) Cross-section
Growth of large area, bulk gallium nitride (GaN) single crystals is of interest due to wide spread application as a substrate for group-III nitride based opto-electronic devices (LEDs, lasers, etc.) and electronic devices (HEMTs, etc.). The current prevalent method for GaN substrate production is through the use of hydride vapor phase epitaxy (HVPE) yielding 2-inch diameter substrates with polar (0001) orientation, threading dislocation (TD) densities of $10^6-10^8 \text{cm}^{-2}$, and c-plane lattice curvatures below 10 m. To further improve device performance and longevity, lower TD density, flatter lattice plane material is needed, in addition to the availability of large area non-polar and semi-polar oriented GaN substrates.

One viable pathway to achieve this target is the ammonothermal method, which has demonstrated 2-inch diameter material of exceptional quality. The basic ammonothermal method dissolves GaN feedstock in a supercritical ammonia solution containing a mineralizer, for example sodium, and recrystallizes the material on a high quality GaN seed. To further improve availability and lower the production cost of the resulting crystal, improved growth rates are needed. Furthermore, reduction in impurity levels is needed to improve transparency for optical based devices.

To that end, an ultra high purity growth environment was created within a Ni-Cr superalloy autoclave by introducing a silver capsule. [1] Silver was found to be stable in the growth environment and did not incorporate into the crystal. As a result of the silver capsule, improvements in growth rate were observed, yielding peak total growth rates of ~ 340 μm/day for the polar planes and 46 μm/day for m-planes. Degradation in crystal quality based on the full width at half maximum (FWHM) of the omega rocking curve using X-ray diffraction (XRD) when compared to the seed crystal was only observed for the Ga-face (0001) growth, presumably due to poor nucleation. Impurity concentrations for transition metals were reduced to < 1E17 cm$^{-3}$, while oxygen concentrations were comparable to those of the HVPE source material (~ 1E19 cm$^{-3}$). Transparency of the crystals improved to 2.2 cm$^{-1}$ at 450 nm.

REFERENCES
GaN-on-GaN™ LEDs and vertical power diodes have demonstrated superior performance compared to their heteroepitaxial counterparts [1]. Bulk GaN substrates grown by vapor-phase techniques have been in routine commercial use for GaN-based laser diodes since 2006 but have limited availability above 2 inch diameter and are expensive. Soraa has developed a novel, high temperature ammonothermal approach for growth of high quality, true bulk GaN crystals at a greatly reduced cost. Soraa’s patented approach, known as SCoRA (Scalable Compact Rapid Ammonothermal) utilizes internal heating to circumvent the material-property limitations of conventional ammonothermal reactors. The SCoRA reactor has capability for temperatures and pressures greater than 650 °C and 500 MPa, respectively, enabling higher growth rates than conventional ammonothermal techniques, yet is less expensive and more scalable than conventional autoclaves fabricated from nickel-based superalloys. SCoRA GaN growth has been performed on 2 inch c-plane SCoRA seed crystals to thicknesses of 3 mm at growth rates greater than 10 μm h⁻¹. These growth rates are significantly larger than those achieved by conventional ammonothermal GaN growth and are sufficient for a cost-effective manufacturing process. The SCoRA GaN crystals have been characterized by a range of techniques, including x-ray diffraction rocking-curve (XRC) analysis, optical microscopy, cathodoluminescence (CL), optical spectroscopy, and capacitance-voltage measurements. The crystallinity of the grown crystals is very good, with FWHM values of 25-80 arcsec. The optical absorption coefficient less than 1 cm⁻¹ at 450 nm and 2 cm⁻¹ at 410 nm has been observed, meeting the requirements for use as native substrate in blue or violet LED devices. Ultralow dislocation densities and variable doping capability are important power electronic applications, and average dislocation densities below 110⁵ cm⁻² and n-type carrier concentrations between 7×10¹⁶ and 3×10¹⁸ cm⁻³ have been achieved [2,3].

Graphene is the ideal two-dimensional material with a honeycomb carbon structure. It has an extremely high carrier mobility, high tensile strength, and high thermal conductivity, which are highly expected in many application purposes. It is widely known that graphene can be epitaxially grown on the semi-insulating SiC substrate. The electronic properties of graphene strongly depend on its structure of the interface. In this study, we grew graphene, functionalized graphene and the two-dimensional carbide materials.

Graphene was grown by thermal decomposition of SiC. We first tried to modify the interface between graphene and the SiC substrate. By heating the SiC substrate in nitrogen atmosphere, the new nitride interface was formed. Due to the nitride interface, the interfacial carrier scattering by the interfacial phonon was successfully suppressed and the mobility at room temperature was improved. Second, we modified the interface by rapid-cooling technique. Graphite and SiC have the negative and positive thermal expansion coefficient, respectively. It suggests that when we rapidly cool the graphene/SiC material, graphene decouples from the SiC substrate, which would lead to the mobility enhancement. Our atomic force microscopy, Raman spectroscopy, transmission electron microscopy revealed that graphene actually decoupled from the substrate. The electron mobility had less temperature dependence. Finally, We grew carbide materials on the SiC. The carbide materials can be also used for graphene growth. The TiC thin film grown on SiC was decomposed to form graphene. Because TiC is a metallic material, the TiC can be utilized for a good electrode with graphene. In addition, boron carbide thin film was also grown on SiC. The boron carbide film on SiC could be decomposed to form heavily boron-doped graphene.

Graphene is the optimal two-dimensional material with a honeycomb carbon structure. It has an extremely high carrier mobility, high tensile strength, and high thermal conductivity, which are highly expected in many application purposes. It is widely known that graphene can be epitaxially grown on the semi-insulating SiC substrate. The electronic properties of graphene strongly depend on its structure of the interface. In this study, we grew graphene, functionalized graphene and the two-dimensional carbide materials.

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2:00 PM - 2:30 PM
TOWARDS AN UNDERSTANDING OF CATALYTIC 2D MATERIAL GROWTH
Invited
Piran R. Kidambi
Massachusetts Institute of Technology, MA

2D material have attracted a lot of research interest due to a range of exciting properties. However, the development of scalable synthesis methods and suitable device integration technologies/pathways are challenges that currently limit commercial exploitation. In this context, chemical vapor deposition (CVD) has emerged as the preferred route for cost-effective, scalable synthesis. While, rapid progress has been made with empirical post-synthesis trial and error based calibrations, growth control remains rudimentary. Complementary in-situ X-ray photoelectron spectroscopy (XPS), in-situ X-ray diffraction (XRD) and in-situ environmental scanning electron microscopy (ESEM), allows for continuous monitoring of the catalyst surface morphology and chemistry, bulk crystallography and gaseous species during CVD. These measurements offer detailed insights into the nucleation and growth mechanisms of these materials; enabling rational process design for high quality material synthesis and allow for the development of integration pathways to interface these materials in devices for commercial applications.

2:30 PM - 3:00 PM
EPITAXIAL GRAPHENE ON SILICON CARBIDE STUDIED BY ELECTRON SPECTROSCOPY
Invited
Thomas Seyller
TU Chemnitz, Chemnitz, Germany

The outstanding properties of graphene (high charge carrier mobility, exceptional mechanical strength, chemical resistance, etc.) suggest various applications in the areas of, e.g., high frequency electronic devices, MEMS, optoelectronics, plasmonics, sensors, or photovoltaics. In general, graphene will be in contact with other materials, be it in the form of electrical contacts, a substrate, or an encapsulation for the purpose of protection and conservation of the device. Thus, the influence of the surrounding materials on the properties of graphene needs to be studied and understood. In the present work, I will discuss three different cases, in which the properties of graphene are strongly modified by other materials. First, I will discuss the doping of so-called quasi-freestanding graphene on H-saturated SiC(0001). I will show that the observed p-type doping is a consequence of the spontaneous polarization present in hexagonal SiC polytypes. Secondly, I will discuss the coupling of graphene plasmons to optically active modes on the substrate, a phenomenon that was observed to be very robust and present even in the case of quasi-freestanding graphene. Finally, I will present resent results on a study of the influence of different contact metals on the electronic structure of graphene.
Detector Materials: Scintillators and Semiconductors (ACCGE) 3

Location: Madison  
Session Chair(s): Stacy Swider, Mariya Zhuravleva

3:30 PM - 4:00 PM  
PURIFICATION AND CRYSTAL GROWTH OF TLBR FOR ROOM TEMPERATURE AND COOLED DETECTORS  
Invited  
Alexei V. Churilov1, Hadong Kim1, Leonard J. Cirignano1, Yaroslav Ogorodnik1, Alireza Kargar1, Paul R. Bennett1, Suyoung Kim1, Guido Ciampi2, Craig Hines2, William Koehler2, Sean O’Neal2, Zhong He2, Adam M. Conway2, Stephen A. Payne2, Sean R. Bishop2, Stuart N. Cook2, Harry L. Tuller2, Kanai S. Shah1  
1Radiation Monitoring Devices, Inc., Watertown, MA; 2University of Michigan, Ann Arbor, MI; 3Lawrence Livermore National Laboratory, Livermore, CA; 4Massachusetts Institute of Technology, Cambridge, MA

TLBr semiconductor γ-ray detectors have attractive properties for spectroscopic detection, such as high density, high atomic numbers, and a band gap suitable for room temperature operation. The photopoint efficiency of TLBr is ~3 times greater than that of CZT for ~1 cm3 size detector at 662 keV. Crystal growth of TLBr is simplified by its low melting point and cubic crystal structure. These properties make TLBr a promising crystal for low cost production and mass deployment of portable radiisotope identifiers. In the last several years, RMD and collaborators focused on solving the issue of detector polarization and degradation under operating conditions. We investigated variations of purification and crystal growth processes, etching recipes, and electrode metals. We found combinations of process parameters preferred for room temperature and cooled (-20 °C) detector operation. As a result, we have achieved a stable continuous operation for over 1.5 years at room temperature with multiple detectors. We will present the current state of the art TLBr detector results, along with purification and crystal growth methods. This work was supported by the U.S. Department of Homeland Security, Domestic Nuclear Detection Office, under the competitively awarded contract HSHQDC-13-C-00070. This support does not constitute an express or implied endorsement on the part of the government.

4:00 PM - 4:30 PM  
CHARACTERIZATION OF PROCESSES CONTRIBUTING TO DEGRADATION OF THALLIUM BROMIDE DEVICES  
Invited  
AMLAN DATTA, Shariar Motakef  
CapeSym, Inc., Natick, MA

Thallium Bromide (TLBr) is a wide bandgap, compound semiconductor with high gamma-ray stopping power. However, performance degradation and the eventual irreversible failure of TLBr devices can occur due to “polarization”, caused by the electro-migration of Ti+ and Br- ions to the electrical contacts across the device. The TLBr crystals were purified and grown at CapeSym, Inc. TLBr melt filtering (in HBr atmosphere) and zone refining processes were implemented for purification of the starting material. Single crystalline stress-free TLBr ingots were grown using the travelling molten zone (TMZ) technique with both flowing gas and closed ampoule configurations. The crystal growth atmosphere consisted of a mixture of HBr, He and H2 gases in proper proportions. Along with polarization, there are a number of scarcely explored processes which renders the TLBr devices unusable for practical purposes. These include but are not limited to degradation of the electrodes with time, changes in residual stress of the TLBr crystals, variations in the surface chemistry, and radiation damage. Several of these processes will be characterized in detail and potential solutions will be provided. As an example, the most critical TLBr device lifetime-controlling factor is the reaction of anode metal with Br. Different anode materials were tried to find the most resilient candidate, using which the device lasted for more than 100 days (til date) under continuous bias. Variations in the electric field due to an applied bias for an extended time in a TLBr crystal results in non-periodic shifts in its performance. The contribution of residual stress in the crystal for changes in internal electric field will be presented. The effects of surface leakage current towards the stability of the TLBr device performance will be discussed. Different potential passivation agents were tested to minimize this surface effect towards the longevity of the device. Several other modifications to the TLBr device fabrication techniques were made and their effects on the long term performance was tested. Radiation damage characterization of the TLBr devices due to its proximity to various sources will also be presented.

4:30 PM - 4:45 PM  
MODELING OF DISLOCATION MULTIPLICATION PROCESS IN BRIDGMAN GROWTH OF CZT  
Alex Galyukov1, Vasif Mamedov1, Vladimir Artemyev2, Vladimir Kalaev2  
1STR US, Inc., Richmond, VA; 2STR Group, Inc., Saint-Petersburg, Russian Federation

Cd1−xZnxCpxTe (CZT) crystals are used for manufacturing of room temperature radiation detectors, IR filters and also used as a substrate for epitaxial growth of HgCdTe (MCT). Quality and performance of devices manufactured using CZT crystals and wafers depend on concentration of crystal defects, such as dislocations, inclusions, grain boundaries, and on homogeneity of defect and Zinc concentration distribution over the crystal volume. Experimental optimization of crystal growth technology is expensive and time-consuming. Accurate and detailed computer models help to significantly reduce the time and cost of process optimization [1]. In current work, we present advanced computer model of CZT crystal growth, which includes multiple novel capabilities. Presented computer model of 90 mm CZT Bridgman crystal growth process created in CGSim software includes transient analysis of growth and cooling stages. In simulations, crystal growth is coupled with the melt convection affected, in turn, by the Zn content. Calculated results also include distribution of Zn concentration in the grown crystal, which allows one to analyze the effect of growth conditions on radial and axial uniformity of Zn concentration.
Plastic crystal deformation due to thermal stresses during growth and cooling stages is taken into account within Alexander-Haasen model [2]. Modifications of crystal growth process are analyzed with respect to dislocation density. Calculated distributions for different process conditions are compared to commonly used criteria of crystal quality: the shape of melt/crystal interface and temperature gradients.


4:45 PM - 5:00 PM
ANALYSIS OF THE GROWTH OF CADMIUM ZINC TELLURIDE BY THE TRAVELING HEATER METHOD
Jeff H. Peterson, Andrew Yeckel, Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

The traveling heater method (THM) has enjoyed particular success for growth of large crystals of cadmium zinc telluride (CZT). In THM, unlike in conventional melt growth, crystalline CZT is grown from a liquid phase that contains excess tellurium. This solvent phase is produced in a liquid zone that is simultaneously dissolving a feed solid while growing single-crystal material as it is moved via a traveling heater. While THM has proven to grow better quality material than competing methods, growth rates in THM are orders of magnitude smaller.

In this presentation, we formulate a comprehensive mathematical model for the THM process, employing a rigorous phase diagram within the framework of a classical crystal growth model that accounts for heat and species transfer, fluid mechanics, and moving, phase-change interfaces. We solve this model via finite-element methods.

We examine parametric process sensitivity to factors such as growth rate, heater profile, and size of the melt zone. In particular, we focus on how the interaction of species segregation and thermal gradients near the solidification interface leads to conditions of morphological instability that limit stable growth. Specifically, we find supercooled liquid regions that arise when mass transport is modified via convective flows driven by a flow structure triggered by the Brunt-Väisälä instability. This classical instability is associated with atmospheric flows that oscillate within a vertically stratified fluid, forming structures such as lee waves behind a mountain range.

In the case of THM, there is a stabilizing vertical stratification in the lower portion of the liquid zone that is established during growth by the axial thermal profile and fluid density. The onset of constitutional supercooling is associated with a change in the structure of the fluid flow shown in the figure below, where computations are presented for increasing zone size under nearly constant thermal conditions. Approaches aimed at ameliorating this instability and achieving faster growth rates are discussed.

Figure: Fluid flow and heat transfer are shown for the traveling heater method (THM) growth of CZT; liquid zone streamlines are indicated on the left, with downward flow at the centerline, and isotherms are shown on the right. The internal waves structure becomes more prevalent with larger zone size. In the largest zone, a counter-rotating vortex forms next to the growth interface. This work has been supported in part by the National Science Foundation, under DMR-1007885, and no official endorsement should be inferred.

5:00 PM - 5:15 PM
ANALYSIS OF SECOND-PHASE PARTICLE MIGRATION IN CADMIUM ZINC TELLURIDE VIA TEMPERATURE GRADIENT ZONE MELTING
Kerry Wang, Andrew Yeckel, Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

Crystals of cadmium zinc telluride (CZT) grown from liquid phases typically exhibit significant populations of large (10 micron and above) tellurium-rich particles that are deleterious to the performance of semiconductor radiation detectors. While the specific formation mechanisms of these particles are not well understood, their presence is unavoidable due to the supersaturation of tellurium controlled by near-equilibrium thermodynamics during growth.

As an alternative to preventing particle formation during the growth process (which may not be possible), an interesting post-growth treatment may provide a means to higher-quality crystals. Namely, these large, tellurium-enriched, secondary-phase particles can be induced to move away from a region of grown crystal and accumulate elsewhere, leaving higher-quality regions that contain far
fewer particles. This accomplished by heating the sample to slightly above the eutectic temperature (the melting point of the second-phase particles) and engineering a temperature gradient across the sample. Under such conditions, the now-liquid particle dissolves on the hot side and re-solidifies on the cool side, with a net effect of migrating toward the hotter region. This phenomenon is termed “temperature gradient zone melting,” or TGZM. Historically, its discovery was motivated by the experience of arctic explorers, who found that newly formed sea ice was not potable due to brine inclusions. However, after 2-3 years of exposure to sunlight, this sea ice could be used for drinking water. In the aging process, brine inclusions migrate to the surface by diurnal heating, thus purifying the ice. Tiller in 1963 devised the first approximate mathematical model to describe inclusion migration via TGZM.

In this presentation, we present the formulation of mathematical models for particle migration via TGZM. We demonstrate that an approximate analytical solution to this model in one spatial dimension well describes the general behavior of particle migration. The analytical solution shows that steady-state migration is not possible, and that, under a constant thermal gradient, the particle velocity and size increase continually with time. Experimental observations are consistent with these predictions. We also describe the implementation of a moving-boundary, finite-element method that solves the model equations with no simplifying assumptions about mechanistic interactions. Initial results provide excellent predictions of particle migration in CZT.

Left: Depiction of model for particle migration in a thermal gradient. Right: Model results for a spherical tellurium particle migrating through solid cadmium telluride.
This work is supported by U.S. Department of Homeland Security, 2012-DN-077-ARI066-02; no official endorsement should be inferred.
EXACT GROWTH RATE MEASUREMENT OF LYSOZYME CRYSTALS BY INTERFEROMETRY UNDER MICROGRAVITY
Invited
Katsuo Tsukamoto¹, Yoshihisa Suzuki², Hitoshi Miura³, Izumi Yoshizaki⁴
¹Tohoku University, Sendai, Japan, ²Tokushima University, Tokushima, Japan, ³Nagoya City University, Nagoya, Japan, ⁴JAXA, Tsukuba, Japan

Growth rate of lysozyme crystals vs supersaturation under microgravity in the international space station has for the first time been compared exactly by interferometry with that in gravity to understand the fundamental difference of growth mechanism in different gravity conditions.

Numerous protein crystals have been grown under microgravity trying to improve the quality of crystals, in which growth rate of the crystals has been regarded to be smaller than that in gravity because absence of convection or flows. However, we found that the growth rate of lysozyme crystals under microgravity is larger by 20-50% than that in gravity in commonly used growth conditions. Discussion will be made why and the importance of the difference of growth mechanism on the quality of protein crystals by analyzing also the shape of spiral hillocks vs supersaturation and the purity of solutions.

SPIRAL GROWTH OF PROTEIN CRYSTALS INDUCED BY FEMTOSECOND LASER ABLATION
Yusuke Tominaga¹, Mihoko Maruyama¹, Hiroshi Y. Yoshikawa¹, Yuki Hayashi¹, Satoshi Nakayama¹, Yoshinori Takahashi¹, Shigeru Sugiyama¹, Hiroaki Adachi¹, Hiroyoshi Matsumura¹, Kazufumi Takano¹, Satoshi Murakami¹, Masashi Yoshimura¹, Yusuke Mori¹

Spiral growth is an effective growth mechanism to grow protein single crystals with sufficient size for obtaining structural data by X-ray diffraction, because crystals growing by the mechanism continue to grow even at low supersaturation. In the spiral growth mechanism, the origin of growth steps is screw dislocations outcropping on the crystal surfaces. Recently, Yoshikawa et al. found out that micro holes formed on the surfaces of tetragonal crystals of hen egg-white lysozyme (HEWL) by laser ablation processing could be starting points of growth steps [1]. In this study, we also used HEWL as a model protein and artificially generated spiral growth hillocks at the micro holes, which were formed by laser ablation processing.

Laser pulses from a Ti: sapphire laser (800 nm, 250 fs, 0.25 µJ/pulse, 1 kHz) were passed through an objective lens (10×, N.A. = 0.4) and focused on the top surface ((110) face) of a tetragonal HEWL crystal (8 days after the nucleation) grown in a solution (35-45 mg/ml HEWL, 3.9 w/v% NaCl, 0.1 M NaAc buffer, pH 4.5). The laser spot was scanned to the vertical direction during the irradiation, and a micro hole was formed on the (110) face (Fig. 1a). Laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM) [2] was employed to observe elementary steps on the (110) face. Twenty-nine hours after the micro hole was formed, spiral growth steps appeared on the (110) face at the micro hole (Fig. 1c). Ninety-six hours after the micro hole was formed, the spiral growth hillock covered the (110) face completely, and the final area was 1700 × 900 µm (Fig. 1d). Next, laser pulses were focused on the side surface ((-110) face) of another tetragonal HEWL crystal (7 days after the nucleation) and a micro hole was formed on the surface, which is crystallographically equivalent to the (110) face. A spiral growth hillock should be generated at the micro hole. After the micro hole was formed, the growth rate of the (-110) face, which was almost ~0 µm/day before the laser irradiation, recovered to 4.9 µm/day.

We succeeded in inducing a spiral growth mechanism of protein crystals, and also confirmed that the growth of the face of the crystal on which a spiral growth mechanism was induced could be promoted.
We recently developed a new method for growing protein crystals in a semi-solid hydrogel.1) Using the method we can crystallize protein crystals with increased mechanical stability, and the crystals give us high resolution of X-ray diffraction pattern. The crystallization technique occasionally increases nucleation probability too much, as a result problems such as size degradation of each crystals and/or generation of polycrystals occur. For resolving the problems, we combined the semi-solid hydrogel crystallization with the stirring technique2) which enables us to decrease the nucleation probability and increase the size of each crystal.

We used hen-egg white lysozyme (HEWL) as a model protein. The solution condition was 25 mg/ml HEWL, 3% NaCl in 0.1 M NaAc buffer (pH 4.5), and the concentration of agarose was 0, 0.5, 1.0 and 2.0 %. Each of solution was dispensed in glass vials with 0.3 ml volume, then stirred at 0, 50, 75 and 100rpm respectively on a specially designed rotary shaker (Fig.1). We counted the number of
crystals five days after the crystallization started. Figure 2 shows the dependency of the number of crystals on the rotation speed of the shaker. As the agarose concentration increased, the number of crystals increased. The noticeable tendency was that the number of crystals decreased when the rotation speed increased, and this tendency was common to all of the agarose concentration. We measured the temporal change of crystal size using the 0.5% agarose condition at stirring conditions of 0 rpm and 50 rpm. The first nucleated crystal of each stirring condition was tracked (Fig.3). Fig.3 shows that the final (after 35 days) crystal size grown with stirring was 1.4 times larger than the crystal size grown without stirring. These results showed that the stirring technique clearly affect the protein nucleation even in a semi-solid gel, and the combination of the semi-solid crystallization with the stirring technique realized large size protein crystals with increased mechanical stability.

1) Sugiyama et al., JACS (2012), 134 (13), 5786.
2) Adachi et al., JJAP (2004), 43 (4B), L522.

Fig.1 A set up of crystallization.
Fig. 2 The dependency of the number of crystals on rotation speed.
Single crystals of Meta nitroaniline (mNA), an organic nonlinear optical material have been grown by slow cooling technique using mixed solvents. The solubility and metastable zonewidth of mNA has been estimated for different temperatures by constant temperature bath with cryostat facility. Induction periods were measured as a function of temperature for various supersaturation ratios. Interfacial energy has been determined using the experimentally observed induction period values and found to be comparable with the theoretical values [1]. Based on the classical theory of homogeneous nucleation, nucleation parameters such as Gibbs free energy, radius of the critical nucleus, the number of molecules present in the critical nuclei and nucleation rate have been studied. The grown crystal was subjected to various characterization analyses. The crystalline nature of the grown crystal was confirmed by single crystal X-ray diffraction study [2] and the lattice parameters were examined by powder X-ray diffraction analysis. The cutoff wavelength and optical transmission property of the grown crystal was analyzed using UV-Vis-NIR spectral analysis, excitation coefficient and optical reflectance were determined. Fourier transform infrared analysis and Fourier transform Raman analysis were analyzed. Nuclear magnetic resonance determines the chemical environment of the grown crystal. From the Photoluminescence spectrum the emission spectrum was studied. The thermal stability of the grown crystal was determined by thermo gravimetric analysis. The dielectric constant and dielectric loss of the mNA crystal were analyzed. The mechanical property of the mNA crystal was subjected to vickers microhardness tester. Work hardening coefficient was determined by using meyer's law. The hardness related parameters such as elastic stiffness constant, fracture mechanics, brittleness index and also yield strength were evaluated. The second harmonic generation measurement shows the nonlinear optical property of the crystal by using Q-switched Nd:YAG laser and the efficiency of mNA is compared to standard reference material KDP [3].

References

Transmission spectrum of mNA crystal
Gallium oxide, β-Ga2O3, is a wide band gap semiconductor material (~4.8-4.9eV), which is being investigated for a range of electronic and electro-optic device applications, with Schottky diodes, MOSFETs, and UV sensors having been demonstrated. It is important to note that large 2" epi wafers are already available commercially from melt-growth methods. Commercial implementation of these devices will require production scale technology for Ga2O3 film deposition. We have demonstrated deposition of uniform Ga2O3 films on multiple 50 mm diameter (0001) sapphire substrates (per run), single 200 mm diameter (100) silicon substrates and small chips of Ga2O3, using a rotating disc metal organic chemical vapor deposition (MOCVD) reactor. Trimethyl gallium and oxygen were used to produce the unintentionally doped Ga2O3 films, which are smooth, optically transparent, highly insulating, and had excellent thickness uniformity. Ga2O3 films deposited on (0001) sapphire at temperatures of at least 600 C and pressures of at least 45 Torr consisted of (201) oriented β-Ga2O3 in the as-deposited state. The beta crystal structure are stable on annealing to 800 C, in either air or nitrogen atmospheres. Ga2O3 films deposited at lower temperatures crystallize to a similar (±201) oriented β-Ga2O3 structure on post deposition annealing at 800 C. The Ga2O3 epitaxial layers show a sharp optical absorption cutoff in the UV region (~250 nm) in correspondence with the expected bandgap. We also investigated a variety of metal contacts (e.g., Ti, Mo, and In) to the films deposited using electron-beam evaporation. Ohmic behavior was observed after annealing at different temperatures up to 1000°C on both Sn-doped (substrates) and highly resistive, unintentionally-doped material. The In contacts tended to be more stable. Ti/Au ohmic contacts were employed on epi-layers to form photodetectors that showed response to UV radiation (253.7 nm) up to 400 times the dark current. We are currently working on additional process chemistries and further characterizing diode devices in the undoped epi material, the results of which will also be reported on.

Metal oxides like Ga2O3, In2O3, SnO2 and ZnO are transparent conducting oxides (TCO) of high industrial relevance, which have been widely applied for fabrication of transparent electrodes in photovoltaic devices, liquid crystal displays and chemical sensors. For such applications the thin oxide films just need to be highly conductive and transparent but in principle, they do not require good structural properties. Recently, there is a great interest in considering these metal oxides as wide band gap transparent semiconducting oxides (TSO’s).

β-Ga2O3 has been widely studied in the last years, emerging as one of the most interesting example in this class of materials. β-Ga2O3 has a large band gap of 4.8 eV and an expected breakdown electric field in the range of ~5 MV/cm. By growing single-crystalline thin oxide films with high crystalline perfection and a controlled carrier concentration level in the range of 1016-1018 cm-3, they open a new class of wide band gap semiconductor, with application in power electronics and as deep UV-detectors. In this contribution we report on the growth of high quality, single-phase β-Ga2O3 layers on (100) β-Ga2O3 substrates. In the focus of this investigation is the incorporation of Sn as a dopant in β-Ga2O3 layers and their electrical properties. The epitaxial growth of β-Ga2O3 was carried out in a commercial vertical MOVPE reactor using triethylgallium (TEGa) and tetraethyltin (TETSn) as organometallic sources and pure oxygen as oxidant. Mg-doped β-Ga2O3 semi-insulating substrates, grown by the Czochralski method, were used. The layers were studied by different characterization methods (AFM, C-V, Hall-measurements, HRTEM, SEM and SIMS). The homoepitaxial grown layers were coherent and monocrystalline. By HRTEM investigations, we identified stacking faults as main structural defect. The surface morphology was atomically smooth with roughness (rms) smaller than 1 nm. By increasing the TESn-flux in the growth chamber from 4.6x10-12 to 6.6x10-10 mol/ min the chemical Sn-concentration in the grown layers increased from 4x1017 up to 2x1019 cm-3. All the layers showed semiconductor behavior. By using Hall-measurements, it was found that while the mobility fluctuates in the range 25-40 cm2/Vs, the carrier concentration increases from 5x1017 cm-3 to 3x1018 cm-3 by increasing the TESn-flux. The highest mobility value achieved was 41 cm2/Vs at a free carrier concentration of 1x1018 cm-3.

4:10 PM - 4:30 PM

GROWTH OF THICK ON-AXIS SiC EPITAXIAL LAYERS BY HALIDE CVD FOR HIGH VOLTAGE POWER DEVICES

Mark Fanton1, David Snyder1, Brian Weiland1, Kathleen Trumbull1, Gregory Pastir1, Cordell Detzer2
1Penn State University, Freeport, PA, 2Penn State University, University Park, PA

There is an increasing need for thick, low cost SiC epitaxial layers for high voltage (>10KV) power devices for various grid level power switching applications. Hallide chemical vapor deposition (HCVD) is a high growth rate, high temperature process ideally suited to meet the requirements for these thick epitaxial layers. SiC layers ranging in thickness from 25-200µm were grown on both 6H and 4H-SiC substrates by HCVD. The 6H polytype is especially interesting in comparison to 4H due to the differences in growth behavior and defect formation, especially with respect to stacking faults and their negative impact on bipolar devices. The epitaxial layers were deposited on the Si-face of N-doped substrates oriented from 0.1 to 0.5 of the <0001> direction. On axis growth is made
possible by the much larger surface diffusion distances at growth temperatures between 1900-2000°C. The Si and C precursors were SiCl₄ and CH₄ respectively in a mixed Ar/H₂ carrier gas. Typical growth rates were 25-50 µ/hr. The impact of growth conditions on carrier concentration, growth surface morphology, and defect densities, especially 3C inclusions will be described. The current-voltage and capacitance-voltage behavior of Schottky diodes fabricated from thick epitaxial layers will be discussed in relation to growth conditions and defect density.

4:30 PM - 4:50 PM
EPITAXIAL GROWTH OF HIGH QUALITY, SELF-SEPARATION GaN CRYSTALS BY USING A NOVEL HIGH TEMPERATURE ANNEALING POROUS TEMPLATE
lei zhang, Jiaoxian Yu, Yuan Tian, Xiaopeng Hao, Yongzhong Wu, Yongliang Shao, Yuanbin Dai, Qin Huo, Baoguo Zhang
State Key Laboratory of Crystal Materials, Shandong University, Jinan, China, Department of Materials Science and Engineering, Qilu University of Technology, Jinan, China

Objectives: In order to reduce the dislocation density of GaN crystals, avoid cracking and separate GaN crystals from substrate, we propose a simple and effective method to solve these problems.

Method: When GaN is exposed to N₂ flow at temperatures higher than 900 °C, the compound is decomposed. The decomposition contributes to the morphological reorganization or the corrosion of GaN material under suitable condition. Based on this mechanism, we have designed a simple technology to fabricate a novel high temperature annealing porous (HTAP) template. There are few reports on the growth of GaN crystals on a high temperature annealing porous template by hydride vapor phase epitaxy (HVPE). In this paper, a MOCVD-GaN/Al₂O₃ (MGA) template was annealed with appropriate annealed conditions to form the porous template. The porous template was used for growing GaN by HVPE.

Results: The GaN crystal was easily separated from the porous template by the assistance of the micron-porous structure. The self-separation GaN crystal grown on porous template showed smaller full width at half maximum (FWHM) of (002) and (102) reflections in HRXRD measurement than that grown on MGA template. The PL results indicate that the optical quality of the GaN crystal on the porous template was improved and the dislocation density was decreased. The Raman results showed that the stress of GaN crystal grown on porous template is much smaller than that on MGA template.

Conclusion: These results shows that crystalline quality of GaN crystals was improved by using the porous templates.

Outcomes: With this technique numerous voids were generated between the GaN crystal and the HTAP template during the growth. And the voids played an important role in the separation of GaN crystal from HTAP template and the reduction of dislocation density in GaN crystals. The microscale lateral overgrowth of GaN above voids also contributes to the reduction of dislocations. This approach has many prospective advantages (simplicity, cost-effective) over current separation techniques. We think it is a very promising technique for fabricating freestanding high-quality GaN crystals.

4:50 PM - 5:10 PM
GROWTH OF GaN ON PATTERN SAPPHIRE SUBSTRATE BY HYDRIDE VAPOR PHASE EPITAXY
Chu An Li, Chien-Te Chiang, Wun-Huei Siang, Chenlong Chen, Chun-Yu Lee, Mitch M.C. Chou
1Department of Materials and Opto-electronic Science, National Sun Yat-Sen University, Taiwan, 2Taiwan Consortium of Emergent Crystalline Materials, Ministry of Science and Technology (MOST), Kaohsiung, Taiwan

Gallium nitride (GaN), a direct bandgap (3.4eV) semiconductor material of wurtzite structure, has been widely used in optoelectronic devices, such as light-emitting diodes (LEDs) and laser diodes [1,2]. However, bulk GaN single crystal growth is difficult, and
therefore the growth of free-standing GaN (FS-GaN) and GaN template by heteroepitaxial method are attracting considerable
interest [3,4]. Pattern sapphire substrate (PSS) has been generally used to be the substrate of GaN heteroepitaxial growth. HVPE is
the well-known method to produce FS-GaN and GaN template with high growth rate, low cost, and low defect, but there are very few
reports of GaN grown on PSS by hydride vapor phase epitaxy (HVPE). This paper reports the GaN single crystal films grown on c-
plane PSS by HVPE. There is no any SiO2 mask or MOVPE layer pre-grown on PSS. The growth behavior of GaN on PSS by
HVPE was very sensitive to the growth condition. Different growth parameters, such as carried gas, V/III, growth pressure, and low
temperature growth are tried. Fig.1 shows the AFM analysis result of the as-grown GaN thin film. The RMS value is 12.432 nm.
XRD analysis result, as shown in Fig. 2, indicates that the as-grown thin film is single crystal film. The FWHM value is 540 arcsec.
TEM analysis result shows that the growth mechanism is closed to epitaxial lateral overgrowth (ELOG). PL analysis indicates that a
strong UV emission at 3.41 eV, and no weak defect-related broad yellow emission band is found. More details will be presented in
the conference.
References

Fig.1 AFM image of GaN thin film on PSS by HVPE
Fig. 2 XRD analysis result of GaN thin film on PSS by HVPE
Macroscopic nanoribbon crystals. The optoelectronic properties of these novel carbon metamaterials are determined entirely by...
those of their individual nanoscale constituents, widely tunable by varying their width, edge orientation and termination, etc. Our results demonstrate avenues for harnessing CVD processes and the powerful toolset of organic and polymer chemistry to produce nanoscale 2D materials, heterostructures, and novel 3D metamaterials that harness carrier confinement.

Monday, August 3, 2015
5:00 PM - 7:00 PM

Poster Session 1

Location: Mammoth
Session Chairs: Candace Lynch, John Geisz, Andrew Allerman

5:00 PM - 7:00 PM

THE GENERAL APPROACH TO THE MODELING OF DEFECT FORMATION IN THE PROCESS OF CRYSTAL GROWTH
Vitalyi I. Talanin, Igor E. Talanin
Zaporozhye Institute of Economics & Information Technologies, Zaporozhye, Ukraine

Recently, we proposed a diffusion model of the formation grown-in microdefects in dislocation-free silicon single crystals [1]. At a conference in Keystone (Colorado, USA), we proposed to use the diffusion model to describe the formation of defect structure both during the crystal growth, well as for crystals after the heat treatments. By using the diffusion model possible to analyze from unified positions of formation and transformation of the defect structure of silicon crystals from growing until the creation of various of devices.

Diffusion model was the basis of specialized information system. Proposed system is a specialized information system which is software of dual-use [2]. On the one hand it is a virtual experimental device for investigation of the processes of defect formation in growing single crystals and devices based on silicon. On the other hand using the software can determine the conditions for crystal growth and its mode of treatment for a well-defined defect structure.

The correction of traditional concepts about the dominant role of intrinsic point defects showed that semiconductor silicon - a highly pure material with the perfect structure - can be considered as the initial model for the construction of theoretical models of defect formation in other semiconductor materials and metals [3]. The obtained mathematical models and methods proposed for their solution in silicon make it possible to formulate and solve many problems on the kinetics of diffusion processes in solids. We believe that the diffusion model has a general character and is applicable to the mathematical description of processes such as precipitation of impurities, void formation, formation of dislocation loops in crystals, and others. The diffusion model provides an adequate description of the interaction between intrinsic point defects and impurities, as well as the modification of a defect-impurity system during cooling of the crystal after the growth [1]. The priority of the processes of high-temperature precipitation is a fundamental feature that determines the overall kinetics of defect formation in highly perfect crystals of semiconductors and metals.


5:00 PM - 7:00 PM
PURIFICATION, STOICHIOMETRY CONTROL AND CRYSTAL GROWTH OF THALLIUM CHALCOHALIDE ROOM TEMPERATURE HARD RADIATION DETECTORS
Wenwen Lin1, Peng Li Wang2, Zhifu Liu3, Bruce W. Wessels2, Mercouri G. Kanatzidis1
1Department of Chemistry, Northwestern University, Evanston, IL, 2Department of Materials Science and Engineering, Northwestern University, Evanston, IL

Driven by the need of high performance and low-cost room temperature x-ray and γ-ray detectors, purification, stoichiometry control and crystal growth of thallium chalcogenide semiconductors is being developed. The thallium iodide selenide (Tl6SeI4) and thallium iodide sulfide (Tl6S8H4) compositions are main focus of our current research. We will present our strategy and results on pre-growth purification, composition control and crystal growth optimization. High quality single crystal ingots obtained from the growth were waferized, polished and subsequently subjected to Co57 γ-ray radiation. The spectroscopy responses were successively improved with respect to the refined crystal growth techniques.

5:00 PM - 7:00 PM
SCINTILLATION PROPERTIES OF CE:GD3(GA,AL)5O12 SINGLE CRYSTALS GROWN BY CZOCHRALSKI METHOD WITH DIFFERENT MG CO-DOPING CONCENTRATIONS.
Kei Kamada1, Aya Nagura1, Martin Nik1, Satoshi Okumura1, Seiichi Yamamoto1, Shunsuke Kurosawa1, Yuui Yokota1, Jan Pejchal2, Yuji Ohashi1, Akira Yoshikawa1
1Tohoku University, Sendai, Japan, 2Institute of Physics AS CR, Praque, Czech Republic, 3Nagoya University, Sendai, Japan, 4Nagoya University, Nagoya, Japan

Scintillators play important roles in a lot of fields such as high-energy physics, medical imaging, geological exploration and homeland security. Oxide materials based on garnet structure single crystals are promising candidates for scintillator applications, because of well mastered technology developed for laser hosts and other applications, optical transparency and easy doping by rare-earth elements. Recently, our group reported about Ce-doped Gd3(Al,Ga)5O12 (Ce:GAGG) single crystal and scintillation response of about ~90 ns at emission around 520 nm, prospective light yield of about 56000 photon/MeV, and density of 6.63 g/cm3. Recently, alkali earth co-doping effects on Ce doped garnet scintillator such GAGG, Lu3Al5O12(LuAG), Y3Al5O12(YAG) were reported and pronounced decay shorting and increasing of light yield on LuAG and YAG were investigated. In this study we investigated relationship between Mg Ce and Ga concentration, and scintillation properties.

Mg2+ co-doped Ce:GAGG single crystals were grown by means of the Cz method using an RF heating system. The rotation rate was 4-10 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. Crystals were grown from a 48mm diameter Ir crucible under Ar with adding x% of O2 atmosphere to prevent evaporation of gallium oxide.
Mg 0.1 mol% co-doped CexGd3-xGayAl5-yO12 (x=0.015, 0.03 and 0.045, y=2.7, 3.0 and 3.3) single crystals were grown by the 1 inch Cz method. Dopant concentrations were analyzed by WDX, ICP-AES and GD-MS. Ce3+ 4f-5d emission was observed at 520nm in all of the samples. The Pulse height spectra of Mg, Ce:GAGG excited by 662 keV gamma-ray of 137Cs at room temperature and measured using a PMT. Light yield was increased with decreasing Ce and Ga concentrations. The x=0.015, y=3.0 sample showed 45000 photon/MeV of light yield and 51ns(70%) and 235ns(30%). The x=0.045, y=3.0 sample showed fastest timing resolution of 200ps. Further results will be reported in my presentation.

5:00 PM - 7:00 PM
ANALYSIS OF A NOVEL BRIDGMAN CRYSTAL GROWTH SYSTEM DESIGNED FOR NEUTRON IMAGING
Yue Wu, Jeff H. Peterson, Didier Perrodin, Gregory A. Bizarri, Edith D. Bourret-Courchesne, Mark Bourke, Anton S. Tremsin, Jeffrey J. Derby
1University of Minnesota, Minneapolis, MN, 2Lawrence Berkeley National Laboratory, Berkeley, CA, 3Los Alamos National Laboratory, Los Alamos, NM, 4University of California, Berkeley, Berkeley, CA

The modeling of crystal growth processes has developed into a tool useful enough to be able to analyze many of the mechanistic interactions and their importance for crystal growth. However, model predictions have thus far been validated only via indirect measurements after growth is completed, such as examination of the compositional field or the distribution of dislocation densities in a crystal after growth. Furthermore, these indirect measures typically require the destruction of the crystal, making such characterization difficult and expensive. In addition, model results are limited in their application toward process optimization, since we have very little fundamental understanding of how microstructural defects arise during growth. For example, we have only a rudimentary understanding of the dynamics associated with phase change, morphological instability, and defect formation processes at the solidification interface.

This poster will present our initial work to develop models to predict crystal growth conditions in a novel real-time, in-situ neutron imaging technique that allows for simultaneously measuring crystal structure, stress, temperature, and composition. Such measurements will provide, for the very first time, the ability to directly validate the sophisticated crystal growth modeling tools that we have developed. Our models will then be used to promote the design of experiments to focus on the most interesting phenomena affecting the crystal growth process. This symbiotic use of models and direct, in situ measurements will provide a path forward to understanding and improving growth conditions for optimized material outcomes. Ultimately, the understanding obtained by validation and focused study of defect formation processes will truly allow the closing of the loop between materials quality and process development.

This work was carried out at the University of Minnesota supported by the U.S. Department of Energy/NNSA/DNN R&D through a subcontract issued by the Lawrence Berkeley National Laboratory (Contract No. AC0205CH11231), no official endorsement should be inferred.

5:00 PM - 7:00 PM
ANALYSIS OF BRIDGMAN GROWTH OF SCINTILLATOR CRYSTALS FOR ADVANCED DETECTION
Chang Zhang, Jeff H. Peterson, Didier Perrodin, Gregory A. Bizarri, Edith D. Bourret-Courchesne, Jeffrey J. Derby
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The future of high-performance, cost-effective scintillator crystals will be driven by the discovery of new materials and the development of viable methods for their scale-up and production. Both of these tasks are made challenging by the profound difficulties associated with crystal growth processes _ macroscopic-scale processes that are designed to induce atomistic-scale order in the single-crystal materials they produce. Indeed, crystal growth processes are notoriously complicated owing to the strong, nonlinear interactions of transport processes of heat, mass, and momentum with phase change phenomena affecting solid-state microstructure and properties.

The Crystal Growth Laboratory led by Edith Bourret-Courchesne in the Materials Sciences Division, Lawrence Berkeley National Laboratory (LBNL), has achieved notable success in the discovery of new scintillator crystals. While this discovery process was challenging in itself, the next step toward utilization, namely the scale-up and production of these crystals, will also entail significant challenges. Currently, the growth of new materials is, in large part, dependent on the intuition of the crystal grower. The cost-effective production of these crystals will require profound increases in size, yield, and quality. Indeed, it has often been estimated that the development time needed to bring a new, crystalline material to market is over a decade. This poster will present initial results on modeling the thermal characteristics of two Bridgman furnaces in the LBNL Crystal Growth Laboratory. CrysMAS (a code developed by the Crystal Growth Laboratory at Fraunhofer IISB) computations of furnace heat transfer will be compared to measured thermal profiles through the furnaces. Preliminary computations using our finite element code, Cats2D, will be presented to highlight the differences in growth characteristics in these furnaces. Of particular interest is the growth of promising, new scintillator crystals for radiation detection. We believe that the synergies of computation and experiment will promote progress in crystal growth that is not attainable by either in isolation. This work has been supported in part by the Department of Energy, National Nuclear Security Administration, under Award DE-NA0002514, and no official endorsement should be inferred.

5:00 PM - 7:00 PM
FABRICATION OF OPTICAL ELEMENT FROM INVERTED SOLUBILITY LITHIUM SULFATE MONOHYDRATE SINGLE CRYSTAL FOR NLO APPLICATIONS
Rajesh Paulraj, Silambasaran A, Ramasamy P
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In the trend for the development of single crystals for second harmonic generation (SHG), LSMH will undoubtedly attract more attention because of its good nonlinear optical coefficient and broad transparency range. In this work, optical quality single crystals of inverted solubility Lithium sulfate monohydrate were grown by a slow heating with seed rotation technique in order to posses bulky prismatic morphology and the significant optical characteristic features of LSMH are analyzed. The UV- vis transmission
analysis reveals its good optical transmission window ranges from 200 nm to 1100 nm. Also, the single shot and multiple shot surface laser damage thresholds are determined to be 44 GW/cm² and 9 GW/cm² respectively for 532 nm radiation. The second harmonic generation of LSMH has been confirmed by Kurtz powder technique. The refractive indices have been measured employing Brewster’s angle method for the range of wavelength and temperature, the values are fitted with Sellmier equations. As the grown LSMH crystal by this method fulfilled all the requirements, which are in general extremely difficult to achieve simultaneously in single system, the efforts are made to fabricate optical elements from LSMH for frequency doubling applications. Type 1 and type 2 phase matching elements were prepared and experimentally analysed. The results will be discussed in detail.

5:00 PM - 7:00 PM
HOMOGENEITY AND ANNEALING STUDY ON CSSRBR3:EU SCINTILLATOR
Matthew Loyd, Luis Stand, Adam Lindsey, Mariya Zhuravleva, Charles L. Melcher
University of Tennessee, Knoxville, TN

Scintillator crystals used for radiation detection in homeland security applications require bulk size crystals. Therefore compositional and scintillation homogeneity is vital for obtaining an excellent energy resolution. CsSrBr₃:Eu is very promising scintillator with a light output of 35,000 ph/MeV, an energy resolution of 4%, and a melting point of ~760°C. Single crystals of this ternary compound is grown via the Bridgman method from the molten mixture of binary halide raw materials, and therefore some compositional non-uniformity may exist in the crystal due to incomplete melt mixing. In this work, differential scanning calorimetry (DSC) was used to study phase homogeneity by comparing melting and crystallization temperatures in different sections of the crystal. In spite of the shown phase uniformity throughout the boule, gamma spectroscopy measurements utilizing a 137Cs source revealed that CsSrBr₃:Eu had two energy peaks at 662 keV. The spectra were recorded with a crystal encapsulated in mineral oil to protect it from degradation. On the first day the gamma ray spectrum showed one peak at channel 285 and another at channel 450. After day 6 there was no evidence of peak position at channel 450. The packaged crystal was removed and annealed in vacuum at 200°C for 24 hours. This experiment showed that after annealing only the higher channel peak remained and light yield was increased by 48 %, when compared to the non-annealed piece. DSC analysis of sections of the CsSrBr₃:Eu boule as well as the packaged crystal showed homogeneity throughout, implying that the secondary peak is due to an non detectable defect that is removed through annealing.

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5:00 PM - 7:00 PM
STUDY OF INGAN/GAN MQWS ON GAN PYRAMIDS TEMPLATE
Xiangqian XIU, Xuemei HUA, Shiying Zhang, Zili Xie, Ping Han, Qingjun Xu, Yongan Li, Dunjun Chen, Peng Chen, Rong Zhang, Youdou Zheng
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InGaN/GaN multiple quantum wells (MQWs) with semi-polar pyramid array have been fabricated by means of a simple and low-cost etch-regrown process. The etched GaN template contains pyramid arrays with well-defined facets by a convenient photo-assisted chemical etching method. The PL spectra reveal the InGaN/GaN MQWs substantially emitted broad electroluminescence spectra with multiple peaks. A negligible blue-shift as a function of exciting laser intensity gives a strong argument for the absence of a built-in electric field in the studied semipolar structures. The high luminescence efficiency of the MQWs is attributed to the effectively suppressed piezoelectric field and potential localization. Spatially resolved cathodoluminescence (CL) experiments are performed to analyze locally the emission properties over the pyramidal structures. CL peak wavelength increase from the bottom to the top of the facet due to the indium diffusion mechanism. In addition, it is found that the cathodoluminescence intensity of the QW is the strongest among the three QWs. The truncated pyramid structures will provide a solution to the highly efficient broadband visible light emitting devices.

5:00 PM - 7:00 PM
ANISOTROPIC ISLAND NUCLATION AND GROWTH DURING OMVPE OF M-PLANE GAN
Carol Thompson⁵, Edith Perret⁶, Matthew J. Highland⁴, Paul H. Fuoss⁴, Anneli Munkholm⁴, Peter Zapol⁵, Stephen K. Streiffer⁶, G. Brian Stephenson⁷
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Non-polar and semi-polar orientations of III-nitride semiconductors have attracted significant interest due to their potential application in optoelectronic devices with enhanced efficiency over those on polar orientations. Complex growth behavior on these orientations has introduced new challenges to overcome for controlled synthesis of desired structures. In particular, the anisotropic surface properties of m-plane GaN [1] are expected to alter the balance between various surface processes. This provides the
motivation for our interest in fundamental and systematic studies of island nucleation and growth on this surface. Using surface x-ray scattering to probe the interface in situ during OMVPE of GaN on single crystal substrates, we have studied nucleation and growth during homoepitaxy on the m-plane (10-10) surface. We observe all three growth modes (step-flow, layer-by-layer, and three-dimensional) as conditions are varied [2]. The boundary between step-flow and layer-by-layer as a function of temperature \( T \) and growth rate \( F \) is shown in Fig 1. We find an apparent activation energy of 2.8 ± 0.2 eV for the growth rate at the boundary. This is similar to the activation energy observed for OMVPE growth of GaAs, and consistent with a large critical nucleus size for islands.

We have also analyzed the diffuse x-ray scattering that appears during growth when islands are present, to obtain the average island spacing and shape anisotropy as a function of \( T \) and \( F \). Both in situ x-ray scattering and ex situ atomic force microscopy are consistent with anisotropic islands elongated by a factor of 10 or more perpendicular to the [0001] direction. We find that the island nucleation spacing in the [0001] direction has a very weak (-1/4) power law dependence upon growth rate, in good agreement with the prediction for anisotropic diffusion in the limit of large critical nucleus size [3].

Figure 1: Growth mode map for m-plane GaN as a function of growth rate \( F \) and inverse \( T \). Filled blue circles mark the layer-by-layer region and open red circles the step-flow region. Apparent activation energy of \( F \) at the layer-by-layer to step-flow boundary, obtained by interpolating between observations at 3 points (crosses), is 2.8 ± 0.2 eV.

determined by the electroconductivity. To find the equilibrium constants of chemical reactions at the melt surface and at gas-metal interface, we use thermodynamic properties of $\text{Al}^{3+}$, $\text{O}^{2-}$, $\text{MoO}^{+}$, $\text{MoO}_{2}^{+}$, and $\text{MoO}_{2}^{2-}$, which allows us to calculate the reaction rates of all considered chemical mechanisms.

Fig.1 illustrates our estimation of the equilibrium composition of ions in the melt as a function of temperature. $\text{AlO}^{+}$ and $\text{OAIO}^{-}$ are predicted to be dominant ions due to the low electroconductivity of molten sapphire. Their percentage decreases with temperature, whereas $\text{Al}^{3+}$ and $\text{O}^{2-}$ mole fractions increase during the thermal dissociation.

The model is applied to Kyropoulos and HEM processes. Mass fractions of $\text{Al}^{3+}$, $\text{O}^{2-}$, $\text{MoO}^{+}$, and $\text{MoO}_{2}^{+}$ in the gas phase and concentration of aluminum converted to bubbles were computed. Computations show fewer bubbles when molybdenum shields are used instead of tungsten ones, which agrees with the experimental data.

Fig.1

5:00 PM - 7:00 PM
LUMINESCENT PROPERTIES OF CE-DOPED GADOLINIUM PYROSILICATE CRYSTALS GROWN BY THE FLOATING ZONE METHOD
Shunsuke Kurosawa, Toetsu Shishido, Takamasa Sugawara, Akiko Nomura, Kunio Yubuta, Yasuhiro Shoji, Rikito Murakami, Yuui Yokota, Jan Pejchal, Yuji Ohashi, Kei Kamada, Akira Yoshikawa
Tohoku Univ., Sendai, Miyagi, Japan

Recently, we have developed a novel oxide scintillator Ce-doped (La,Gd)$_2$Si$_2$O$_7$ (La-GPS) and discovered its excellent scintillation properties. The emission wavelength of La-GPS crystal was 390 nm, and it has a high light output of approximately 35,000 photons/MeV, good energy resolution (FWHM) of 5.0% at 662 keV, and fast decay time of 46 ns. Moreover, this material has no hygroscopic nature and small intrinsic background. Here, we have developed new materials for a scatter part of the Compton camera, and low-effective-atomic number materials are requirement. Thus, Y-admix La-GPS, Ce-doped (Gd, La, Y)$_2$Si$_2$O$_7$, was grown by Floating Zone (FZ) method; The starting materials were highly pure 99.99% CeO$_2$, Gd$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$ and SiO$_2$ powders which were used for preparation of two sintered bars. Then, these bars were set in the FZ apparatus (FZ-ASGAL) and melted by the focused heating with a pair of high-intensity infra-red lamps and ellipsoidal mirrors. We succeeded in growth the crystal with a few mm size, and optical and scintillation properties of this crystal were investigated The sample excited by alpha-rays and X-rays had emission wavelength around 370 nm, while La-GPS has that around 390 nm. These emission were originated from Ce$^{3+}$ 5d-4f transition, and the wavelength shift was due to the modification of crystal fields. Light output of this Y-admix La-GPS had over 10,000 photons/MeV. We report the crystal growth of this sample and its luminescent properties in this presentation.

5:00 PM - 7:00 PM
Z SCAN STUDY OF HYDROXYETHYLAMMONIUM P-NITROPHENOLATE SINGLE CRYSTAL
NAGALAKSHMI RAMAMOORTHI¹, Sudharsana N¹, Srinivasan Padmanabhan²
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1:00 PM - 5:00 PM
Z SCAN STUDY OF HYDROXYETHYLAMMONIUM P-NITROPHENOLATE SINGLE CRYSTAL

The study of dielectric properties of layer TiGaSe2 single crystal in frequency range \( f = 5 \times 10^4 - 3.5 \times 10^7 \) Hz allowed to establish relaxation character of dispersion of dielectric permittivity and nature of dielectric losses. It was shown that frequency dependence of the dissipation factor tan \( \delta \) is due to relaxation polarization. The relaxation frequency \( f_r = 8.8 \times 10^5 \) Hz and relaxation time \( \tau = 1.1 \times 10^6 \) s have been estimated for TiGaSe2. The ac-conductivity across the layers of studied crystals varies with frequency as \( \sigma \sim f^{0.8} \) which is characteristic for hopping conductivity near the Fermi-level states. Density of localized states at Fermi level \( NF = 7.5 \times 10^{18} \) eV\(^{-1}\)cm\(^{-3}\), the energy spread of these states \( \Delta E = 5 \times 10^{-3} \) eV, average hopping time \( \tau = 1.2 \times 10^{-6} \) s and distance \( R = 240 \) Å have been evaluated for TiGaSe2 single crystal.
Z scan study of hydroxyethylammonium p-nitrophenolate single crystal
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Abstract: Novel organic hydroxyethylammonium p-nitrophenolate single crystals have been grown by slow evaporation method for the first time. From the single crystal X-ray diffraction study, it was found to crystallize in the monoclinic system with a centrosymmetric space group which favours third harmonic generation. The optical property was carried out using ultraviolet-visible and photoluminescence spectroscopy techniques. The grown crystal was characterized using Fourier transform infrared, Raman and nuclear magnetic resonance spectroscopy. The thermal stability was investigated by using thermogravimetry, differential thermal analysis, derivative thermogravimetry and differential scanning calorimetric analyses. Z-scan studies revealed that the compound exhibits reverse saturable absorption and positive nonlinear refraction.

Keywords: Crystal growth; X-ray diffraction; Z-scan; Optical property; Thermal property.

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GROWTH AND OPTICAL SPECTROSCOPY OF RARE-EARTH DOPED POTASSIUM LEAD HALIDES FOR POTENTIAL APPLICATIONS IN INFRARED LASERS AND RADIATION DETECTORS

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The luminescent properties of rare-earth doped solids have been under intense exploration for various applications ranging from displays and lasers to scintillators. Potassium lead chloride (KPb₂Cl₅) and potassium lead bromide (KPb₂Br₅) materials have recently emerged as new non-hygroscopic laser hosts with low maximum phonon energies (~138-203 cm⁻¹), which lead to small non-radiative decay rates for trivalent rare earth dopants. In this work, the material synthesis, purification, crystal growth, and spectroscopic characterization of rare-earth (Pr³⁺, Ce³⁺, and Eu²⁺) doped potassium lead halides were investigated for possible applications in infrared lasers and radiation detectors. The synthesis of studied materials was based on the careful purification of starting materials including multi-pass translation in a zone-melting system and halogenation. The growth of the purified materials was then carried out through vertical Bridgman technique using a two-zone furnace. The trivalent praseodymium ion (Pr³⁺) offers a large number of laser transitions in the visible and infrared spectral regions. Using ~1.45 um and 1.9 um pumping, IR emissions at ~1.6, ~2.4, and ~4.5 μm were observed from Pr doped KPb₂Cl₅ and KPb₂Br₅ corresponding to the 4f-4f transitions of 3F⁴/₃→3H⁴, 3F₂/3H₆→3H⁴, and 3H₅→3H₄, respectively. Optical properties of the ~1.6 um Pr³⁺ transition including infrared to visible upconversion emission studies were discussed. Under Xenon flash lamp excitation, preliminary spectroscopic results showed allowed 5d-4f Ce³⁺ emission centered ~375 nm in Ce³⁺ doped KPb₂Cl₅. Moreover, commercial Ce:YAG and Ce:YAP crystals are included in this study for comparison. Detailed spectroscopic results including time-resolved excitation and emission, temperature dependent emission studies as well as scintillation properties of the investigated crystals will be presented at the conference.

CATALYST FREE GROWTH OF III V NANOWIRE ARRAY ON SI

Jae Cheol Shin, Chan Ho Choi
Yeungnam University, Kyeongbuk, Korea, Republic of

We report catalyst-free growth of III-V nanowire array on silicon (Si) substrate grown by metalorganic chemical vapor deposition. The InAs nanowire array has been uniformly grown on entire 2 inch Si wafer with the maximum number density of 2 × 10⁷/cm² without any metal catalyst or pattern assistance. In addition, the ternary InAsₐPₜ nanowire array shows a uniform alloy composition across the nanowire, as confirmed by photoluminescence, X-ray diffraction, and z-contrast scanning transmission electron
microscopy analysis. Cross-sectional TEM image confirms a heterogeneous interface between III-V nanowires and Si. Several optical and electrical devices have been demonstrated using these catalyst-free III-V nanowires on Si platform. The wafer-scale, heterogeneous III-V nanowires are promising for low-cost fabrication of nanowire-based devices on Si platform.

5:00 PM - 7:00 PM
**INVESTIGATION ON STRUCTURAL AND NONLINEAR OPTICAL SPECIFICITY OF BIOLOGICAL AMINO ACID CRYSTALS**

*Xu Dong, Liu Xi Tao, Zhang Guang Hui, Wang Lei, Wang Xin Qiang, Ren Quan*

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Natural amino acids is the basic unit of biological protein in organism, which participates in the function of the life. Some amino acid salt crystals also are important non-linear optical materials possessing sole specificities. In invertebrates, Phosphate Arginine (PA) has been known as the medium carriers for bio.-energy storage and transport by means of convertible transition between adenosine diphosphate (ADP) and adenosine tri-phosphate (ATP), but in vertebrates, Phosphate Creatine (PC) as it.

L-arginine phosphate monohydrate (LAP) crystal has the similar structural unit as PA. It was discovered as an excellent nonlinear optical (NLO) crystal with one and only or outstanding properties, such as high conversion coefficients (over 90%); extremely high laser-induced damage threshold (63 GW/cm² at 1053 nm and 1 ns); projecting stimulated Brillouin scattering (SBS) properties; etc. Energy storage in organism and laser-induced damage in crystals are both correlative to energy. In order to explore the relationship between them, a series of investigations were carried out.

Absorption spectrum of LAP crystal indicates the relatively high absorption coefficient (especially in 1064 nm). Thus, the extremely high laser-induced damage threshold of LAP crystal should be inconsistent with high energy absorption. The nuclear magnetic resonance (NMR) and fluorescence emission spectra of LAP and various amino salt solutions have been investigated. The results show that L-arginine and phosphate may affect the state of the molecular under the energy action in the solution.

Temperature dependence X-ray diffraction (XRD) and solid state NMR spectroscopy were performed to study the impact of energy (heat and magnetic) fields on LAP crystal. XRD results reveal that LAP processes a reversible specific phase transition as the temperature changed. Several new diffraction peaks appeared when the temperature kept at 90°C for a period of time, while the peaks disappear when the temperature decreased to a low temperature for a long time. Saturation recovery experiments show that the crystal has a long proton spin-lattice relaxation time (1H T1) of 184 s, which is much larger than other crystals. The results show that LAP crystal has an amazing solid-state stability. The guanadyl group is strongly engaged with phosphate group through hydrogen bonds, and the specific interactions involving the two groups may be the important influence on the laser-induced damage and physical properties.

A series of novel amino acid salt crystals, have also been studying and some new results of crystal growth and properties will be reported.

5:00 PM - 7:00 PM
**GROWTH, OPTICAL AND DIELECTRIC PROPERTIES OF A SEMI-ORGANIC SINGLE CRYSTAL: MORPHOLINIUM DIHYDROGEN PHOSPHATE**

*Rajan Babu D, Arul H, Ezhil Vizhi R*

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Engineering of new nonlinear optical materials, structures and devices with the enhanced figure of merit has developed a major force to drive nonlinear optics from the laboratory to real time applications [1]. Incorporation of an inorganic additive with an organic molecule provides high optical nonlinearity, chemical flexibility, thermal stability and excellent transmittance in the visible region. Morpholinium is a strong alkali, which can be considered as a kind of secondary aliphatic amine [2]. The incorporation of dihydrogen phosphate ion into six member ring of morpholine makes the molecule a good nucleophile. Morpholinium dihydrogen phosphate single crystals was synthesized and subsequently grown by slow evaporation technique at room temperature for nonlinear optical applications. The grown crystal has been subjected to single crystal X-ray diffraction to confirm the structure. The crystal belongs to the monoclinic system with the space group P2₁ [3]. The UV-Vis-NIR spectroscopic study was carried out on the grown crystal and it shows good optical transparency in the entire visible region with a minimum cut-off wavelength of 269 nm. Optical band gap was computed as function of photon energy using Tauc’s plot as 4.32eV. Refractive index of the grown crystal was determined using Metricon Prism Coupler. Dielectric studies were carried out for various frequencies at different temperatures. Dielectric constant, dielectric loss and AC conductivity were calculated and plotted as a function of frequency at different temperatures. The value of activation energy for ionic migration was calculated using Arrhenius plot. The second harmonic conversion efficiency was determined using Kurtz-Perry powder technique and the efficiency was found to be 1.4 times greater than that of standard KDP.

5:00 PM - 7:00 PM
**THE EFFECT OF ND DOPING LEVEL ON THE SPECTRAL PROPERTIES OF ND:GGG CRYSTAL**

*Zhitai Jia, Chunming Dong, Jun Shu, Wenxiang Mu, Yanbin Li, Xutang Tao*

State Key Laboratory of Crystal Materials, Shandong University, Ji Nan, China

In recent years Nd:GGG crystal, as an excellent candidate for high power laser applications, has attracted lots of attention owing to its good mechanical properties, excellent thermal conductivity and high efficiency laser performance. In comparison with Nd:glass, Nd:GGG boasts a better mechanical strength and higher thermal conductivity which, as a result, can achieve the goal to rapidly cool the gain media between runs and reduce the turnaround time between laser firings. Regarding to Nd:YAG, one of the most excellent gain media for solid-state lasers, Nd:GGG crystal can be grown more easily with larger diameter and higher doping level, which is very important for high power laser design.

Since 2004 our group has been engaged in growing Nd:GGG crystals with different diameters (25, 50, 70, 130, 156, and 178 mm) by Czochralski method at State Key Laboratory of Crystal Materials, Shandong University. Large-sized Nd:GGG crystals with the diameter of 190 mm were successfully grown recently, as shown in fig. 1 below. In addition, the optical homogeneity of as-grown
Nd:GGG crystal was tested. The homogeneity value of $4.10 \times 10^{-5}$, with a RMS of $5.41 \times 10^{-6}$, was obtained, indicating that the as-grown crystal is of high quality. In order to optimize the Nd concentration inside the crystal, we also analyzed the relationship between the Nd doping levels and the thermal and spectral properties of Nd:GGG crystals. Concerning the laser results, a laser power up to 10000 Watt has been obtained from our $\Phi 5$ mm Nd:GGG samples. All the results show that Nd:GGG crystal should be a promising laser material for high power laser in future.

5:00 PM - 7:00 PM
SINGLE CRYSTAL GROWTH OF GALLIUM OXIDE BY EFG METHOD
Wenxiang Mu, Zhitai Jia, Xutang Tao
State Key Laboratory of Crystal Materials, Shandong University, Ji Nan, China

β-Ga2O3 is a transparent conductive oxide with the bandgap of 4.8eV, and attracts more and more attention in recent years, because it has a lot of new applications include: deep ultraviolet photodetectors, photodiodes, transparent thin film transistors, light-emitting diodes (LEDs), Schottky diodes, high voltage transistors and high temperature gas sensors. β-Ga2O3 crystal has been grown for several decades by various techniques such as: Verneuil technique, floating zone technique, flux method, chemical vapor transport. But it is hard to get high quality and large size β-Ga2O3 crystal by these methods. Z. Galazka et al. have grown 2 inch β-Ga2O3 crystal with good crystal quality by Cz method in 2014, and they also have done the High-Voltage Field Effect Transistors by using their β-Ga2O3 crystal. And the Japanese scientists have grown this crystal by the edge-defined film-fed growth (EFG) method, and the crystal wafer with 2 inch is already commercial now. The devices, like LED and power device, have been studied already. We have chosen the EFG method to grow the β-Ga2O3 single crystal, since it is convenient for the growth of high quality β-Ga2O3 single crystals. In this method the Ir-particles, floating on the surface of the melt, do not disturb the growth process and the growth interface is stable. Crystals can be pulled up at a higher speed, 10-30mm/h, with comparatively lower energy consumption than Cz method. However, until now there is no detailed works reported about the controlling of the temperature gradient near the top of the Ir die, Ga2O3 raw material decomposition and volatilization, and the Ir crucible erosion, during the crystal growth process. In this work, we have grown β-Ga2O3 crystal with 25 mm width by the EFG method, as shown in fig. 1. Especially we have checked the possible ways, like the growing atmosphere, the temperature gradient, and so on, to reduce the decomposition of Ga2O3 at high temperature and to protect the iridium crucible. The grown crystal has been checked by the high resolution X-ray diffraction, and the FWHM was 43.2 arcsec, which showed good crystal quality. And we are also finding the suitable conditions for the crystal processing because of its fragile and plate like habitual nature, like the cutting and polishing, especially for the chemical mechanic polishing to achieve good β-Ga2O3 substrates.
HORIZONTAL DIRECTIONAL SOLIDIFICATION OF ZN BASE ALLOYS
Alicia E. Ares
CONICET/UNaM, Posadas, Argentina

HORIZONTAL DIRECTIONAL SOLIDIFICATION OF ZN BASE ALLOYS
A. E. Ares a, b, *

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b Materials Institute of Misiones, IMAM (CONICET - UNaM).

Abstract
Ingot defects may originate from several sources: foreign materials in the melt stock or electrode, drop-in material from the furnace interior, and solidification defects. To eliminate each of these, it is first necessary to characterize their features, understand formation mechanisms, and determine rates of formation or dissolution. Solidification defects in particular depend on the local solidification environment as well as thermal and compositional perturbations to the solidification zone.

In this paper the behavior of thermal parameters (cooling rates, temperature gradients and velocities and accelerations of the interphases) was studied, analyzing the obtained grain or crystal structures in the samples after solidification, in order to relate the properties of the Zn-base alloys when they are solidified in a horizontal device by extracting heat in two opposite directions.

In addition, the Niyama numbers, Ny, were determined in these alloys, which are related to the macroporosity. Ny are critical numbers from which the macroporosity in the samples is evident.

STUDY OF THE COLUMNAR-TO-EQUIAXED TRANSITION FROM THE GROWING OF A LITTLE NUMBER OF COLUMNAR GRAINS
Alicia E. Ares
CONICET/UNaM, Posadas, Argentina

STUDY OF THE COLUMNAR-TO-EQUIAXED TRANSITION FROM THE GROWING OF A LITTLE NUMBER OF COLUMNAR GRAINS
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Abstract
Pb-Sn alloys were directionally solidified in order to obtain a small quantity of crystals (i.e. single crystal, bi-crystals or three crystals) and then the columnar-to-equiaxed transition (CET) during directional solidification process. The local temperature was measured and the temperature gradients and cooling rates were calculated. Comparing the position of the CET between structures and the thermal conditions it was found that the transition occurred in Pb-2wt.%Sn bicrystals when the temperature gradient in the melt at the liquidus temperature was between -3.76 °C/cm and -1.11 °C/cm. It was found that the undercooling in the liquid needs to be ~3°C for the nucleation and growth of the equiaxed grains in front of the columnar growth.

A DEFECT STUDY OF CZOCHRALSKI GROWN YAG CODOPED WITH CERIUM AND CALCIUM
Understanding defects in scintillating and laser materials is a critical pathway in improving photo-peak resolution and increasing their yield and efficiency. Cerium (III) doped yttrium aluminum garnet (YAG) and Cerium (III) doped Lutetium Oxyorthosilicate (LSO) have long been used as scintillators. In addition, Ce:LSO is commonly codoped with calcium which increases light output and improves scintillator lifetime. This improvement has been previously attributed to calcium eliminating oxygen vacancies in the crystal through some authors have noted that there is likely a more complex relationship between the vacancies and light output. In order to better understand calcium’s effects in scintillating crystals, several cerium and calcium codoped YAG crystals were grown using the Czochralski method.

Three Ce:Ca:YAG crystals were grown by the Center for Materials Research at Washington State University. Cerium concentration was held at 2.0 at.%, while calcium was varied at 0, 0.25, and 1 at%. The radioluminescent (RL) light output and decay time performance were measured on photo multiplier tubes using a 137Cs source. Results showed that calcium greatly improved the lifetime from 115 ns down to 70 ns though the light output and photo-peak resolution degraded. Photoluminescence (PL) revealed that the light output at cerium’s 530 nm peak is significantly reduced which is consistent with RL results, though PL showed an even greater reduction than RL did. Absorption measurements showed the presence of a large UV absorption peak with calcium codoping. This absorption peak has been previously attributed in Ce:Ca:LSO to Ce4+. To confirm Ce4+ formation, X-ray Absorption Spectroscopy (XAS) using Superconducting Tunneling Junctions was performed with synchrotron radiation at the Advanced Light Source. XAS showed that Ce4+ was formed which explains the absorption peak and decreased light output.

Thermoluminescence (TL) showed significant reduction in charge carrier traps (similar to Ce:Ca:LSO) which indicates either a decreased number of traps or that calcium provides a non-radiative decay pathway. Work by Stanek et al. showed that when doping with a 2+ valence ion in YAG, the most likely defect clusters all include oxygen vacancies. Thus, it is expected that calcium codoping with a lower number of vacancies, in contrast to TL results. This was confirmed using Positron Annihilation Spectroscopy which showed significant increase in the vacancy concentration with increasing calcium concentration. All of these results suggest that Ca addition to Ce:YAG reduces light output and increases vacancy concentration, but also interacts with charge carrier recombination rates, improving the scintillators lifetime.

5:00 PM - 7:00 PM  
GROWTH AND SCINTILLATION PROPERTIES OF CE DOPED YAG SINGLE CRYSTAL  
Yuui Yokota, Shunsuke Kurosawa, Yuji Ohashi, Kei Kamada, Akira Yoshikawa  
Tohoku University, Sendai, Japan

We have developed a growth method of shape-controlled single crystal YAG by a micro-pulling-down (µ-PD) method in order to decrease the manufacturing cost. The shape-controlled growth method enables to make the crystal elements with the shape of final device element. In this study, we have developed the shape-controlled Ce doped Y3Al5O12 (Ce:YAG) scintillator crystals for the radiation detector. Shape-controlled Ce:YAG crystals were grown by the µ-PD method using Ir crucible with a 5×5 mm2 square die at the bottom. Starting materials, Al2O3, Y2O3, CeO2 powders (> 4N), were mixed as nominal compositions, (Y1-xCe)xAl5O12 x = 0–0.06, and the mixed powders were entered into the crucible. The crucible was heated by a high-frequency induction coil up to the melting point of YAG and crystal growths were performed using undoped YAG crystal as a seed. Chemical compositions of grown crystals were evaluated by the electron probe micro analysis. Transmittance spectra were measured by the spectrophotometer. Pulse-height spectra under γ-ray excitation were evaluated by the photomultiplier tube (PMT).

Transmittance spectrum of as-grown Ce:YAG crystal without polishing. It indicated more than 80% in the wavelength range of 500 - 900 nm. In addition, it showed a clear photo-peak under γ-ray irradiation in the pulse-height spectrum. The light yield was sufficient for the application of dosimeter.

The shape of grown crystal was controlled by the die of crucible and the shape was the square bar with 5×5 mm2 cross sectional surface along to the growth direction. In addition, facets were generated on the surface of as-grown crystals by conforming the shape of die to the crystal orientation of seed crystal. The as-grown crystals indicated high transparency without polishing due to the facet surfaces.

In the transmittance spectrum of as-grown Ce:YAG crystal without polishing, the as-grown crystal indicated more than 80% in the wavelength range of 500 - 900 nm. In addition, it showed a clear photo-peak under γ-ray irradiation in the pulse-height spectrum. Other properties of the shape-controlled Ce:YAG crystals will be reported.

5:00 PM - 7:00 PM  
PHASE FORMATION, STABILITY AND CRYSTAL GROWTH OF CERIUM ACTIVATED SOLID SOLUTION OF GD2Si2O7 AND LU2Si2O7  
He Feng1, Wusheng Xu1, Zhijun Zhang1, Xu Zhan1, Jingtai Zhao1, Fang Lei1  
1Shanghai University, Shanghai, China; 2GE Global research, Shanghai, China

Recently, due to the outstanding scintillation performance of gadolinium pyrosilicate Gd2Si2O7:Ce (GPS:Ce) and its incongruently melting characteristic, the study on crystal growth of GPS:Ce has been gaining more and more attention. The rare earth ions cerium and lanthanum are reported to can effectively stabilize the crystallization behavior of GPS melt. In this paper, the lutetium ion was chosen to evaluate its impact on the GPS:Ce crystallization behavior. The pure pyrosilicates and their solid solutions were synthesized through solid state sintering method under temperatures between 1100 and 1650 °C. The phases formation and transitions of (Gd1-xLu)xSi2O7 (x=0-1) solid solution were determined by X-ray diffraction and Raman spectra. The phase of (Gd1-xLu)xSi2O7 was discussed and established. And according to the result of phase stability region, single crystal of (Gd1-xLu)xSi2O7:0.1%Ce was successfully prepared by floating zone method (as shown in the inset of the figure) and the differential scanning calorimeter was used to confirm the Lu ion effect during crystallization behavior of GPS. The rare earth lutetium should be a candidate for improving the crystallization behavior of GPS and further work should be carried out on determining the optimal content of lutetium for balancing the GPS:Ce crystal growth and its scintillation performance.
CRYSTAL GROWTH AND SCINTILLATION PROPERTIES OF LU SUBSTITUTED CEBR3 SINGLE CRYSTALS

Tomoki Ito\textsuperscript{1}, Yuui Yokota\textsuperscript{1}, Shunsuke Kurosawa\textsuperscript{3}, Kei Kamada\textsuperscript{4}, Jan Pejchal\textsuperscript{5}, Yuji Ohashi\textsuperscript{1}, Akira Yoshikawa\textsuperscript{6}

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Halide single crystals show relatively high light yield and energy resolution because of the small band-gap. Among these halide materials, CeBr\textsubscript{3} crystal has fast decay time of \(~19\) ns in addition to the high light yield \(~60,000\) ph/MeV and the CeBr\textsubscript{3} crystal is expected to be applied in radiation detectors with high timing resolution. We have reported the growth of CeBr\textsubscript{3} and Pr doped CeBr\textsubscript{3} crystals grown by a modified micro-pulling-down (\(\mu\)-PD) method that can be used to grow fiber crystals of halide hygroscopic materials at faster growth rate than conventional methods.

In this study, we focused on Lu substituted CeBr\textsubscript{3} crystals in order to increase its density and effective atomic number which are very important factors for applications in the gamma-ray detector. Especially, probability of the gamma-ray interaction with matter is proportional to the forth to fifth power of the effective atomic number. Lu with larger atomic number than Ce can be substituted for Ce site of CeBr\textsubscript{3} crystal. Therefore, we grew the Lu substituted CeBr\textsubscript{3} crystals with various Lu concentrations by the modified \(\mu\)-PD method and investigated their scintillation properties.

The mixed powders with the nominal compositions of the (LuxCe\textsubscript{1-x})Br\textsubscript{3} \((x = 0.00, 0.01, 0.05, 0.10, 0.20, 0.30)\) were prepared in the glove box and their crystals were grown by the modified \(\mu\)-PD method. Phases and chemical compositions of the grown crystals were measured by the powder X-ray diffraction and inductively coupled plasma analysis, respectively. Specimens for optical and scintillation measurements were prepared by cutting and polishing the grown crystals. The light yields and decay times were evaluated with \(^{137}\)Cs radiation source.

During the crystal growth by modified \(\mu\)-PD method, at first, the moisture was completely removed by the baking process. Then the carbon crucible with the mixed powder was heated up by high-frequency induction coil and the crystals were grown by pulling the melt with the Pt-Rd seed from the die of the crucible. The pulling rate was about \(0.05\) mm/min and the shape of the meniscus was controlled by the power of the high-frequency induction coil.

(\(\text{Ce},\text{Lu}\))Br\textsubscript{3} crystals with transparent parts were successfully grown by the modified \(\mu\)-PD method in the \(x\) range of \(0 \sim 0.10\). The light yield of Lu10mol\% substituted CeBr\textsubscript{3} crystal was one-fourth of that of the CeBr\textsubscript{3} crystal. On the other hand, it showed a relatively high energy resolution. The details of crystal growth and scintillation properties will be reported.
THE STUDY ON LIGHT EXTRACTION EFFICIENCY OF LIGHT EMITTING DIODE WITH GRADED-INDEX PHOTONIC CRYSTALS
Ping Ma, Hongxi Lu
Institute of semiconductors Chinese academy of sciences, Beijing, China

We report on the fabrication of GaN-based light emitting diodes incorporating high extraction efficiency photonic crystals with graded refractive index. The optical structure consist of one photonic crystal layer and one graded-index layer. The photonic crystal layer diffracts guide mode light to radiation mode. The graded-index layer is helpful to light extraction for the refractive index decreased gradually from gallium nitride to air.

5:00 PM - 7:00 PM

FE-TE-SE BASE SUPERCONDUCTING MATERIALS SINTERED BY A NEW EXPLOSIVE METHOD
Fengying Wang¹, genda gu²
¹North University of China, Taiyuan, Shanxi, China, ²Brookhaven National laboratory, upton, NY

We have made a number of Fe-Te-Se polycrystalline materials by a new explosive method. The high pure Fe, Te and Se elements were sealed in thick steel cell with TNT explosives. The maximum pressure and temperature inside the steel cell are 30 GP and ~800 oC, respectively when the explosives was ignited at 400 oC. We have sintered a number of the FeTe1-xSex polycrystalline crystal materials (x ≤ 0.6) by using explosive method. The effects of the explosive condition and the compositions of a FeTe1-xSex has been studied. The crystal structure and superconductivity of FeTe1-xSex materials have been studied.

5:00 PM - 7:00 PM

"CHEMICAL WEATHERING" EXFOLIATION OF ATOM-THICK TRANSITION METAL DICHALCOGENIDES AND THEIR ULTRAFAST SATURABLE ABSORPTION PROPERTIES
Yongzhong Wu, Gang Zhao, Shuo Han, Aizhu Wang, Mingwen Zhao, Zhengping Wang, Xiaopeng Hao
Shandong University, Jinan, China

Two-dimensional (2D) transition metal dichalcogenides are attracting increased attention because of their excellent electronic and optical properties. Inspired by the natural weathering exfoliation of seaside rocks, we propose a “chemical weathering” concept for fabricating atom-thick 2D materials from their bulk counterparts. We experimentally demonstrated that chemical weathering-assisted exfoliation mechanism was a simple and efficient method of preparing atom-thick MoS2 and WS2 monolayers. These monolayers are difficult to prepare using other approaches. Interestingly, the as-prepared MoS2 and WS2 monolayers exhibited excellent saturable absorption and mode-locking properties in all-solid-state lasers because of intermediate states resulting from S-vacancy defects. The obtained passively Q-switched laser operation with 60 ns pulse width and ultrafast mode locking with 8.6 ps pulse width were promising for all-solid-state laser application.

5:00 PM - 7:00 PM

THE DEPOSITION OF SiCN BUFFER LAYER FOR 3C-SiC GROWN ON SI SUBSTRATE
Ping Han, Xiaolong He, Zheyang Li, XuZhao Chai, Shu Fan, Le Yu, Le Huang, Tao Tao, Zili Xie, Xiangqian Xiu, Xuemei Hua, Hong Zhao, Rong Zhang, Youdou Zheng
China

Silicon carbonitride, with an adjustable band gap between 2.86 and 5.0 eV, is considered as one candidate for fabricating advanced blue or ultraviolet optoelectronic devices. The SiCN film can also be a suitable buffer layer for 3C-SiC grown on Si substrate since the SiCN with 5 % nitrogen concentration possess the same structure as 3C-SiC and has the lattice constant of 0.4345 nm closing to the 3C-SiC. The SiCN layer has been deposited on Si(111) substrate by a chemical vapor deposition (CVD) system in this work. The substrate has been carbonized at temperature of 1100°C in C₂H₄ atmosphere before the deposition. The carbonized silicon substrate and ammonia(NH₃) were used as C, Si and N sources, respectively. The growth temperature T₉ amounted to 1380°C. The X-Ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results indicate that the deposited film possess the same structure as 3C-SiC with around 6.0 at.% N substituting for C and the main chemical bonds in SiCN are Si-C, Si-N. From the surface of the SiCN layer to substrate, the silicon content linearly increases from 47.2 at. % and the carbon content linearly decreases from 43.1 at. %. Such a distribution of Si and C content is resulted from diffusion of the atoms during the epitaxial growth at high temperature. The 3C-SiC epi layer has been grown on the SiCN/Si(111) successfully. The crystallinity of SiC is obviously improved comparing with that directly grown on Si(111) substrate.
Fig. 1 XRD spectra from SiCN/Si(111). Inset: XRD spectra from SiC/Si(111), SiCN/Si(111).
Fig. 2 XPS sputter depth profile and the evolution of the chemical bonding states of SiCN/Si(111)
The Silicon (Si) based integrated circuit (IC) technology has undergone an impressive development over the last decades. The main driving force for the increase in chip performance was the aggressive reduction in CMOS device size facilitated by the good material properties of Si and Silicon dioxide. Nowadays this miniaturization of planar devices has reached physical limits and new device architectures are introduces such as FinFET, Gate-all-around nanowire devices and TFET. A further boost in device performance is expected by the implementation of new channel materials with higher carrier mobility than Si and for this reason III/V materials have attracted much interest of late.

However, the potential integration of III/V materials to the current highly perfected Si CMOS technology is accompanied by several challenges. Due to the large lattice mismatch of most interesting III/V candidates, such as InGaAs, InAs and GaSb, to Si it is of key importance to follow an integration path, which leads to a low misfit defect density in the active III/V layer. In addition any considered III/V device architecture has to meet the requirements of the next technology node, which is beyond the 14nm-node. The monolithic growth of III/V materials on patterned Si wafers offers an integration scheme towards the high requirements on both material quality and scaling. The deposition of lattice-mismatched III/V materials between shallow trench isolations (STI) with high aspect ratio leads to an efficient trapping of threading dislocations in the lower region of the trench whereas the top layer has a high crystal quality (aspect ratio trapping (ART)).

But the application of very narrow trenches with less than 50nm width also rises new aspects, which need to be carefully investigated: For example the oxide removal from the Si surface in the trench bottom before III/V growth, the precursor diffusion/transport into the trenches and the relaxation behavior as a function of trench width and orientation. The topic of the presentation is an introduction to selective area growth on patterned Si wafers. MOVPE growth characteristic and material quality as well as the relaxation mechanism regarding the InGaAs/GaAs material system will be presented. Finally possible application routes will be discussed.

There are no III/V semiconductors with high electron mobility which can be grown lattice matched on Si (001)-substrate. Thus, Sb-based materials, such as Ga(PSb), that are grown highly mismatched on Si substrates are discussed as specific relaxation buffers for high electron mobility n-III/V channel layers like (GaIn)As or (GaIn)Sb. The defect formation within these layers has to be understood in detail with respect to defect type, defect concentrations as well as surface morphology to optimize the layer structures for later device applications.

The Ga(PSb)-buffer layers are grown by metal organic vapor phase epitaxy (MOVPE) systematically varying the growth conditions and are investigated in detail by several TEM (transmission electron microscopy) techniques. A specific lattice-matched GaP layer is grown in between the Si substrate and the metamorphic buffer so that the challenges due to the charge neutrality at the GaP/Si-interface and the annihilation of antiphase boundaries are taken into account. The strain induced by the high mismatch should relax by misfit dislocations at the GaP/PSb-GaP-interface. In addition, dark-field and high resolution TEM show that the bulk may contain other defects like stacking faults, twins and threading dislocations depending on the used growth conditions. High-angle annual dark-field scanning TEM investigations of the interface reveal that the misfit dislocations are mainly Lomer dislocations and 60° dislocations pairs. The obtained correlation of structural defect formation as a function of MOVPE growth conditions will be reported and discussed.
Towards the Integration of In53Ga47As on 300 mm Si for CMOS Sub 7 nm Node: Development of Thin Graded InGaAs Buffers

Yves Mols¹, Bernardette Kunert¹, Gweltaz Gaudin², Robert Langer¹, Matty Caymax¹
¹imec, Leuven, Belgium, ²Soitec, Bernin, France

High-mobility In53Ga47As is a promising alternative channel material for Si in high-performance CMOS logic scaling to sub 7 nm node. Integrating high-quality In53Ga47As on 300 mm silicon is very challenging due to 8% lattice mismatch. This can be accommodated by a compositionally-graded InGaAs buffer. Traditionally, such buffers have low grading rates and, hence, need several micrometers to achieve low threading dislocation density (TDD). However, device processing requirements and cost considerations demand a much thinner buffer (≤ 1 µm), imposing very aggressive grading rates, which bring the risk of phase separation in the InGaAs alloy. As can be seen in the time-temperature-transformation (TTT) curve in Quitoriano and Fitzgerald [1], low growth temperatures and fast growth rates suppress phase separation. Here we report on the development of high-quality graded InGaAs buffers deposited on 2” GaAs substrates in a 300 mm industrial manufacturing MOVPE reactor as first step (only 4% lattice mismatch!); a next paper will report the ongoing work on 300mm silicon substrates. Initially, we studied 2 µm low-indium (16%) InGaAs buffers (0.57% misfit/µm) grown at 640 °C and 530 °C with different growth rates. No phase separation and low TDD ≤ 1.1·10^6 cm-2 (as determined by TEM) are revealed for 640 °C whereas for 530 °C phase separation and much higher TDD are seen. Hence, based on the TTT-curve, we then focused on increased growth rates at 530 °C as well as lower deposition temperature, i.e. 450 °C. We target an In50Ga50As layer on 1 µm buffer which means a grading rate of 3.54 % misfit/µm, significantly higher than the maximum grading rate used by Fitzgerald’s group (≤ 2.43 %) in their thick multi-temperature multi-
material buffers [1] and approaching Takano’s 4% misfit/μm for InGaAs grown at 450 °C [2]. Cross-sectional TEM of the 530 °C grown buffer (figure left) shows no phase separation whereas at 450 °C (figure right) some scarce indications of phase separation are found. Plan-view TEM is ongoing to estimate the TDD. For comparison, higher growth rate experiments at 640 °C are also ongoing. Extensive characterization (TEM, XRD, AFM) and benchmarking will be discussed at the conference. In conclusion, this simple one-micron one-material one-temperature buffer approach on GaAs is a first critical step in paving the path towards integrating high-mobility In53Ga47As on silicon for sub 7 nm node scaled CMOS.


8:30 PM - 8:50 PM
PSEUDOMORPHIC GROWTH OF DIRECT BAND GAP Ga(NAsP) ON Si (001)
Peter Ludewig
d, Stefan Reinhard
d, Tatjana Wegele
d, Kakhaber Jandieri
d, Andreas Beyer
d, Kerstin Volz
d, Wolfgang Stolz
d
1NAsP III/V, Marburg, Germany,2Philipps-University Marburg, Germany

The integration of optical components on Si is desirable for the improvement of the performance of Si-based CMOS devices and to benefit from reduced energy dissipation and faster data transmission. However, there is still no efficient light source for this application as Si as an indirect semiconductor is not suitable for efficient light emission. The novel material Ga(NAsP) is a promising candidate to overcome this problem since it can be deposited pseudomorphically strained on Si with a direct band gap and, furthermore, low temperature lasing operation was already demonstrated. In order to further improve quality of this novel material, Ga(NAsP)/(BGa)(AsP) multi quantum well (MQW) structures were deposited on ex. Si (001) substrates with GaP nucleation layer using metal organic vapor phase epitaxy (MOVPE). Triethyl gallium (TEGa), tertiarybutyl phosphine (TBP), tertiarybutyl arsine (TBAs) and unsymmetrical dimethylhydrazine (UDMHy) were used as precursors for Ga, P, As and N, respectively. The growth temperature and gas phase ratios were varied over a wide range and the influence on the composition, morphology and optical properties of the Ga(NAsP) QW was studied. Therefore high resolution x-ray diffraction, photoluminescence spectroscopy, atomic force microscopy and scanning transmission electron microscopy measurements were applied. In contrast to other dilute nitride materials, such as (GaN)NAs), the N incorporation in Ga(NAsP) is constant over the temperature range from 550°C to 650°C. The P content, however, clearly decreases at lower temperatures, which is related the higher stability of the TBP in comparison to TBAs and UDMHy. Furthermore, it was found that the QW becomes rougher, the higher the growth temperature is set. Finally, optimized growth parameters were found, at which smooth hetero interfaces and strong direct band gap PL of the Ga(NAsP) QW was observed, which could be used as active material in monolithically integrated laser on Si in future.
Tuesday, August 4, 2015
8:00 AM - 10:00 AM

Young Author and AACG Awards

Location: Missouri
Session Chair(s): Tom Kuech, Chris Wang

8:30 AM - 9:15 AM
THE SCIENCE OF MODELING THE ART OF CRYSTAL GROWTH
Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

The art of growing large, single crystals from liquid phases ranks among the most challenging of materials processes. Indeed, crystal growth process development, operation, and optimization requires a thorough understanding the complex interplay of nonlinear transport and phase change phenomena that drive crystal growth. From a modeling and simulation perspective, these problems are among the most complex and challenging ever attempted and require a multidisciplinary approach drawing on a wide range of scientific and engineering expertise. This lecture will provide some perspectives on how modeling has impacted crystal growth understanding and practice. Research vignettes from our prior modeling of melt and solution growth systems will be presented, and future challenges will be discussed.

9:15 AM - 10:00 AM
YOUNG AUTHOR AWARD: NEW HORIZONS IN COMPLEX OXIDE THIN-FILM GROWTH: DESIGNING NEXT-GENERATION, HIGH-PERFORMANCE MATERIALS
Lane W. Martin
University of California, Berkeley, Berkeley, CA

Complex oxide materials possess a range of interesting properties and phenomena that make them candidates for next-generation devices and applications. But before these materials can be integrated into state-of-the-art devices, it is important to understand how to synthesize and, ultimately, control the response of these often complex materials in a deterministic manner. In this talk we will discuss the science and engineering advanced thin-film deposition of these materials. We will explore the role of the epitaxial thin-film growth process and the use new types of lattice mismatch strain to engineer properties in electronic and ferroelectric materials. As part of this, we will discuss how slight variations in film stoichiometry can play an important role in the evolution of thin-film strain and properties in a number of systems. From there, we will investigate how new manifestations of epitaxial constraint can enhance electric field, stress, and temperature susceptibilities (i.e., dielectric, piezoelectric, pyroelectric, and electrocaloric effects) in ferroelectrics. The presentation will highlight the role of advanced crystal growth methodologies in developing an understanding of stimuli-induced response, designing new high-performance materials, controlling phase and domain/microstructure state to isolation, understand, and produce enhanced responses, and much more. In particular, we will explore three examples of how we can push the boundaries of modern thin-film growth and epitaxial strain to control materials, including: 1) the production and use of strain gradients in compositionally-graded materials, 2) the use of film orientation to produce exotic domain structures and responses, and 3) “defect strain” pathways to push the limits of strain control of materials.

The Young Author award is presented to someone under 35 years of age who has shown outstanding achievement in the field of crystal growth/epitaxy/modeling primarily through published papers. The Young Author award also comes with a plaque and $500.
OXYGEN IMPURITIES IN METAL-HALIDE SCINTILLATORS
Stacy E. Swider, Stephanie Lam, Shariar Motakef, Amlan Datta
CapeSym, Inc., MA, CapeSym, Inc., Natick, MA

Scintillators are an important class of materials used in detection of gamma radiation in applications including medicine and homeland security. A large number of metal-halide scintillators crack during crystal growth and cooldown. Precursors for metal-halide crystalline scintillators are known to be deliquescent and to contain oxygen impurities. These impurities, in turn, are believed to form oxylides that become a source of cracking and yield loss in the final crystal. Crystal growers have developed a number of techniques to reduce oxygen impurities, such as zone refining, melt fritting, and gettering via cation dopants. However, establishing the maximum allowable concentration of oxygen in these materials has proven difficult. Optical methods of oxygen measurement, such as IR transmission through the crystal, require very long sample lengths. Other optical methods such as Raman can become dominated by non-informative surface states. Therefore, the halide-salt precursor industry has traditionally relied on combustion analysis, wherein evolved oxygen is measured in an IR cell. We have installed a combustion analysis system (ELTRA) in a glove box at < 1 ppm moisture, and determined the lower detection limit of the system to be 7 ppm wt, which equals 150 ppm mol oxygen in a material such as SrI2. The oxygen concentration in metal-halide precursors and grown crystals was found to be close to this 7 ppm detection limit, impeding our ability to optimize oxygen purification techniques.

To better understand oxygen behavior, we experimented with adding oxygen to our assays. We conducted partial-pressure mass-spectroscopy experiments (RGA) using YCl3 with 2% Y2O3. The RGA instrument recorded evolution of chlorine-oxygen compounds at the onset of melting, and the partial pressure of these volatiles increased with temperature. These volatile species disappeared once the charge was re-frozen. Condensed volatiles were collected and measured in the combustion system. It recorded 30 times more oxygen in the sublimed material than in the remaining, re-frozen charge. The re-frozen charge, in turn, contained 100 times less oxygen than the 2% oxygen which had been intentionally added. These results suggest that the very process of melting helps release oxygen-compounds. During growth in sealed ampoules, the released oxygen compounds accumulate and may result in a corresponding equilibrium in the melt, causing formation of cracks in the grown crystal. We will report on these experiments other considerations in oxygen removal, including use of halide overpressure to prevent loss of stoichiometry, and the implications of these results on the crystal growth process.

NUMERICAL MODELING OF SCINTILLATOR PROPORTIONALITY AND LIGHT YIELD FROM EXPERIMENTALLY AND COMPUTATIONALLY DETERMINED HOST AND DOPANT PARAMETERS
Richard T. Williams, Xinfu Lu
Wake Forest University, Winston-Salem, NC

We report a model of proportionality and total light yield in scintillation materials that takes into account the strong radial gradients and varying excitation density characteristic of electron tracks in order to predict proportionality and light yield in intrinsic hosts as well as doped scintillators, and as a function of temperature. The model allows visualizing where (spatially and in time) the light originates, where charges are trapped, and how the carriers migrate in hot, thermalized, and self-trapped states. The diffusion-limited coupled rate equations listed below are solved in cylindrical track geometry to predict proportionality from the capture rate constants and transport coefficients. Made progressively more inclusive of physical phenomena over the last 3 years [1-2], the model is now in validation studies that predict for the first time electron response from independently determined material parameters in tested cases of halide as well as oxide scintillator systems. Modeling of undoped CsI and CsI:Tl at 295 K as well as undoped CsI at 100 K [3] will be described, where the same model fits all three behaviors. YAP:Ce is being modeled in the same way and models of co-doped scintillators are planned.
Carrier capture rates, nonlinear quenching rates, and carrier transport coefficients for the model parameter inputs are measured by picosecond absorption [4], laser interband z scan of nonlinear quenching [5], and time-resolved photoconductivity.

Acknowledgment: Supported by DHS DND, NSF Grant 2014-DN-077-ARI-077 and NNSA DNN R&D subcontract from LB15-V-AdvDetMater-PD2JJ. This support does not constitute express or implied endorsement on the part of the Government.


11:00 AM - 11:15 AM
SCALE-UP AND COMMERCIALIZATION OF CLYC SCINTILLATION CRYSTALS
Joshua Tower, Patrick O’Dougherty, Craig Hines, Rastgo Hawrami, Chuncheng Ji, Jaroslav Glodo, Kanai Shah
Radiation Monitoring Devices, Inc., Watertown, MA

The scintillator Cs2LiYCl6:Ce (CLYC) has been developed as a dual-mode detector for neutrons and gamma rays. CLYC offers fast isotope identification due to its good energy resolution, as well as simultaneous detection of neutrons with high sensitivity. Discrimination between gamma ray and neutron signals can be effectively achieved through pulse height or pulse shape techniques. We report on recent efforts to scale-up the crystal growth processes for CLYC. Radiation Monitoring Devices (RMD) has established production processes for growth of 3" diameter CLYC crystals that are used for radiation security instruments. Crucial elements of the CLYC process include pre-purification of the raw materials, careful control of stoichiometry and doping, and vertical Bridgman growth conditions. One of the main challenges has been to reduce defects such as cracks, grain boundaries, and inclusions. We will review the development of CLYC with emphasis on the current state-of-the-art and commercialization progress.

11:15 AM - 11:30 AM
COZCHRALSKI GROWTH OF 2INCH CE-DOPED (LA,GD)2Si2O7 SINGLE CRYSTALS FOR SCINTILLATOR APPLICATION
Akira Yoshikawa1, Shunsuke Kurosawa1, Yasuhiro Shoji1, Valery I. Chani4, Rikito Murakami1, Kei Kamada1, Yuui Yokota5, Yuji Ohashi4, Vladimir Kochurikhin6
1IMR and NICHe, Tohoku Univ., C&A Corp., Sendai, Japan, 2IMR and NICHe, Tohoku Univ., Sendai, Japan, 3IMR, Tohoku Univ., C&A Corp., Sendai, Japan, 4IMR, Tohoku Univ., Sendai, Japan, 5NICHe, Tohoku Univ., Sendai, Japan, 6C&A Corp., General Physics Inst., Sendai, Japan

Ce-doped gadolinium pyrosilicate (or disilicate), Ce:Gd2Si2O7 (Ce:GPS) crystals have also high light output of 30,000 photons/MeV and FWHM energy resolution of 6.0% at 662 keV at room temperature. Moreover, it shows high temperature stability and it is suitable for natural resource survey. However, Ce:GPS melts incongruently. Therefore, it has to be grown from the solution (flux). As an example, Ce:GPS crystals were grown from the melt heavily doped with Ce (approximately 10 at.% regarding Gd host cations to be substituted) in order to modify the phase diagram and to stabilize the crystal growth process. Such excessive Ce-concentration leads to reduced light output because of self-absorption or concentration quenching. On the other hand, optimal Ce⁺⁺ content with respect to the amount of host
rare-earth cations is approximately 0.75-2.50 at.%. Unfortunately, this amount of Ce³⁺ is not sufficient to improve stability of the GPS formation.

Some of the other disilicate crystals formed by small rare-earth metals including Lu₂SiO₅, Yb₂SiO₅, and Er₂SiO₅, melt congruently. However, undoped Gd₂SiO₅ cannot be produced from the melt of its stoichiometric composition. It melts incongruently at 1720°C with decomposition to orthosilicate Gd₂(SiO₄)₂ and liquid phase. For that reason, simple solidification of Gd₂SiO₅ stoichiometric melt results in formation of non-desired Gd₂(SiO₄)₂ phase that melts congruently.

In this study, Ce-doped lanthanum-gadolinium pyrosilicate (La₂Ce,Gd)₂SiO₅ (Ce:La-GPS), crystals with various content of rare-earth elements were produced from the melt, and their optimal La/Gd ratio was examined. It was found that Ce:La-GPS single crystals of acceptable optical quality can be produced from the melts ranging from La₂-Gd₂SiO₅ to La₂-Gd₂SiO₅ and containing about 1 at.% Ce with respect to the host rare-earths of La and Gd. The crystal growth was performed by the micro-pulling-down and Czochralski methods. The crystals were chemically uniform along the growth axis and their composition was equal to that of the melt, thus corresponding to vicinity of congruent melting composition. Spatial distribution of Ce in La-GPS was also inspected, and no variation of Ce content was detected as a result of its similarity to one of the host cation (La) regarding the size. 2inch Ce-doped (La₂,Gd)₂SiO₅ single crystals were grown by the Czochralski method.

Basic optical and scintillation properties of the Ce:La-GPS crystals are also reported, and it is demonstrated that partial substitution of Gd with La has no negative impact on crystal growth and physical performance of the crystals.

11:30 AM - 11:45 AM
GROWTH AND SCINTILLATION PROPERTIES OF ALKALI METAL AND CE CO-DOPED LU3AI5O12 SCINTILLATOR
Kei Kamada¹, Vladimir V. Kochurikhin², Martin Nikl³, Shunsuke Kurosawa¹, Jan Pejchal¹, Yuui Yokota¹, Yuji Ohashi¹, Akira Yoshikawa¹
¹Tohoku University, Sendai, Japan,²General Physics Institute, Moscow, Russian Federation,³Institute of Physics AS CR, Prague, Czech Republic

Oxide materials based on garnet structure single crystals are promising candidates for scintillator applications because of well mastered technology developed for laser hosts and other applications, optical transparency and easy doping by rare-earth elements. The Ce-doped Lu3Al5O12 (Ce:LuAG) single crystal was shown to be a prospective scintillator material with a relatively high density of 6.7 g/cm³, a fast scintillation response of about 60-80 ns (due to the 5d-4f radiative transition of Ce³⁺ providing the emission around 500-550 nm), and light yield of about 12-14,000 photons/MeV. Silicate scintillator such Ce:LSO and Ce:LYSO single crystals co-doped with Ca²⁺ and Mg²⁺ have been recently investigated and improvement in their scintillation characteristics, namely afterglow suppression and scintillation decay acceleration, were claimed which is based on the suppression of such slow delayed recombination processes. Positive role of stable Ce⁴⁺ centres has been proposed in to explain the improved scintillation performance of Mg-doped LuAG:Ce optical ceramics. Its light yield was enormously enhanced and the presence of Ce⁴⁺ was clearly identified by its characteristic charge transfer (CT) absorption in the near UV range below 350 nm. The aim of this work is to investigate and compare the A⁺ (≡Li⁺, Na⁺ and K⁺) co-doping effects on luminescence and scintillation properties of Ce:LuAG single crystal scintillator.

A stoichiometric mixture of 4N MgCO₃, CaCO₃, Li₂CO₃, K₂CO₃, Na₂CO₃, CeO₂, αAl₂O₃ and Lu₂O₃ powders was used as starting material. Namely, starting powders were prepared according to the formula of (AxCe₀.005Gd₁-x)₃Al₅O₁₂(CO₃)(x=0.0002, 0.0005, 0.001) single crystals of A (≡K, Na, and K) co-doped Ce:LuAG were grown by the 𝜇-PD method with an RF heating system.

Optical, luminescence and scintillation properties such as absorption, excitation and emission spectra, and light yield and decay time were evaluated. All of the grown crystal showed Ce³⁺ emission band at 520nm. In addition of the 4f-5d1,2 absorption bands of Ce³⁺ center at 450 and 340 nm, respectively, the smooth Ce⁴⁺ CT absorption below 350nm is clearly enhanced with increasing concentration of only Li. Light yield was increased by Li co-doping. The Li (x=0.0001) sample showed the highest light yield of 24000 photo/MeV, which is around 200% of light yield of the non co-doped crystal. Fast and slower decay components were accelerated by Li co-doping. Absorption, emission spectra, light yield and scintillation decay time of K and Na co-doped sample are comparable to the non-co-doped crystal.

11:45 AM - 12:15 PM
RECENT DEVELOPMENTS IN HALIDE SCINTILLATORS
Edith Bourret-Courchesne
Lawrence Berkeley National Laboratory, Berkeley, CA
Tuesday, August 4, 2015
10:30 AM - 12:00 PM

Fundamentals of Crystal Growth (ACCGE) 4

Location: Jefferson
Session Chair(s): Katsuo Tsukamoto

10:30 AM - 11:00 AM
INTEGRATED PHASE-FIELD CRYSTAL APPROACH TO INVESTIGATE INTERFACE TENSION AND NUCLEATION BARRIERS
Invited
M. Ajmal Choudhary¹, Julia Kundin¹, Martin Oettel², Heike Emmerich¹
¹Materials and Process Simulations, University of Bayreuth, Bayreuth, Germany, ²Institute of Applied Physics, University of Tübingen, Tübingen, Germany

The Phase-field crystal (PFC) modeling has emerged as a computationally efficient tool to address crystal growth phenomena on atomistic length and diffusive time scales. Here, we use a two-dimensional phase-field crystal model for a binary system based on Elder et al. [Phys. Rev. B 75, 064107 (2007)] to study critical nuclei and their liquid-solid phase boundaries, in particular the nucleus size dependence of the liquid-solid interface tension as well as of the nucleation barrier. The motivation behind is to thereby establish a new methodological approach, that can get hand on interfacial energies beyond classical predictions - as relevant in a whole range of crystal growth applications. Critical nuclei are stabilized in finite systems of various sizes, however, the extracted interface tension as function of the nucleus radius r is independent of the system size. We find a phenomenological expression to describe the dependence of the extracted interface tension on the nucleus radius r for the liquid-solid system. Moreover, the numerical PFC results show that this dependency can not be fully described by the nonclassical Tolman formula. Additionally we focus on the impact of the underlying solid-liquid dividing surface definition on the interfacial energy and its relevance in conditions based on the interfacial energy as the Young's one.

11:00 AM - 11:15 AM
NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS OF CU SOLIDIFICATION
Luis A. Zepeda-Ruiz
Lawrence Livermore National Laboratory, Livermore, CA

The development of predictive theories for the study of non-equilibrium phase transitions occurring in dynamic materials processes, such as shocks, requires a multi-scale approach that spans from the atomistic to the continuum scale. For this purpose, we present results of Non-equilibrium Molecular Dynamics (NEMD) simulations of solidification of Cu from the melt for both, thermal cooling and compression conditions. The interatomic potential is modeled within an Embedded Atom Method framework. Our NEMD simulations show a transition from spinodal-like to nucleation-dominated phase transition as a function of both cooling and compression rates. In addition, the phenomena of nucleation and growth of the fcc phase, as well as the appearance and effects of bcc wetting layers, are discussed.
11:15 AM - 11:30 AM
GROWTH KINETICS AND BULK GROWTH OF INVERTED SOLUBILITY LITHIUM SULFATE MONOHYDRATE SINGLE CRYSTAL AND ITS OPTICAL CHARACTERIZATION
Rajesh Paulraj, Silambarasan A, Ramasamy P
SSN College of Engineering, Kanchipuram, India

Nucleation and growth kinetics give valuable information about the crystal growth process, which can be employed in the growth of large size crystals. Accordingly, this work discusses nucleation theory as applied to crystallizing inverted solubility lithium sulphate monohydrate (LSMH) crystals. It is shown that the classical approach explains the available nucleation data under most conditions used for growing LSMH crystals. LSMH will undoubtedly attract more attention because of its good nonlinear optical coefficient and broad transparency range. We have established a procedure to grow high quality bulk size single crystals of LSMH by unidirectional crystallization Sankaranarayanan - Ramasamy (SR) method. The grown LSMH crystal by this method fulfilled all the requirements, such as a second harmonic response and excellent crystal characteristics including large crystal size with desired facets, higher laser damage stability, superior optical quality, wide transparency range and controllable crystal thickness, which are in general extremely difficult to achieve simultaneously in single system. The results are discussed in detail. Therefore, the LSMH crystals could emerge as a potential candidate for the applications in laser photonics and optoelectronic devices.
The strength of the coordination bonds developed between the cation and the anionic or neutral organic molecules comprises the functional groups like -CH2, -COOH will be in between that of noncovalent interactions and carbon-carbon bonds of majority of the organic compounds [1]. Nucleation and growth kinetics give valuable information about the crystal growth process, which can be utilized in the growth of large size crystals. Hence we made an attempt to study the nucleation kinetics such as solubility, metastable zonewidth, induction period and in turn the nucleation parameters namely interfacial tension, Gibbs critical free energy, radius of critical nuclei were computed. Induction period was measured by isothermal method for the saturation temperature by varying the degree of supersaturation. As a result of it good quality crystal was grown by adopting slow cooling solution growth technique. Single crystal XRD evidences that lithium succinate crystallized in trigonal crystal system with centrosymmetric space group R3[2]. The presence of functional groups were confirmed by FT-IR analysis. Optical transmittance were analyzed by recording UV-Vis-NIR spectrum which shows that the grown crystal exhibits maximum transmittance in the UV and Visible region with a cutoff wavelength 227.5 nm. Band gap energy was estimated as 5.95 eV with the aid of Tauc’s plot. Reflectance and extinction coefficients were studied as a function of photon energy, the results reveals that the crystal can be tailored for device fabrication. Nonlinear optical property was examined using Q-switched Nd-YAG laser and it was observed that the frequency conversion efficiency of Lithium Succinate is 3 times that of KDP. Vicker’s microhardness test reveals that the crystal exhibits Reverse Indentation Effect and it falls under soft material category with Meyer’s index number 4.1. The other mechanical parameters such as elastic stiffness constants, fracture toughness, brittleness index and yield strength were computed. From thermal analysis, it is found that the grown crystal is stable up to 242.74 °C. Dielectric nature of lithium succinate were studied as a function of frequency at different temperature to understand the polarization schemes.

References

Crystal structure of Lithium succinate
OMVPE FROM FIRST PRINCIPLES - REALISTIC QUANTUM-CHEMICAL MODELS FOR GROWTH AND PROPERTIES
Invited
Ralf Tonner
Philipps-Universität Marburg, Marburg, Germany

Elementary processes in all steps of OMVPE can have a crucial influence on the quality of the resulting films. In many cases, these key steps are hardly understood or experimentally inaccessible (e.g. reaction barriers). We employ quantum chemical computations, mainly density functional theory with dispersion correction, to shed light on these elementary processes in different phases of OMVPE. For the first step - the gas phase decomposition of precursors - we find very high barriers for several reactions proposed earlier for TBP and TEGa[1] and unusual reaction mechanisms relevant for ligand design.[2] The gas phase mechanism was also found to be relevant for the surface-assisted decomposition steps.

In a joint endeavour of experiment and theory, we could reveal the thermodynamic and kinetic reasons for the unusual appearance of GaP/Si interfaces. Intermixing models established previously are not sufficient to explain the pyramidal structure observed experimentally. Instead, relative facet stabilities and adatom mobilities in the interface region need to be quantified to find a rationale for the atomistically-resolved measurements.[3]


IN SITU OBSERVATION OF THE GAP/SI(100) HETEROINTERFACE FORMATION
Sebastian Brueckner, Oliver Supplie, Matthias May, Andreas Naeglelein, Peter Kleinschmidt, Thomas Hannappel
TU Ilmenau, Ilmenau, Germany

Tandem absorbers composed of Si as bottom cell and a III-V material with a bandgap between 1.6 and 1.8eV are close to optimum for photovoltaic operation as well as solar watersplitting devices. Pseudomorphic GaP buffer layers with high crystal quality can be grown on Si(100) applying a pulsed low temperature nucleation. The atomic structure of GaP/Si(100) heterointerfaces is decisive regarding its electronic properties for the III-V/Si device performance, but its formation is still not understood. According to ab initio calculations, compensated interfaces exhibit lowest formation energies, but we indirectly found indications for a kinetically limited abrupt interface formation with Si-P bonds applying in situ reflection anisotropy spectroscopy (RAS) [1].

Here, we start our studies with well-defined, almost single-domain Si(100) surfaces in D$_4$ configuration, where the Si dimers are aligned in rows parallel to step edges [2]. We analyze changes in the dielectric structure during subsequent GaP nucleation time-resolved with RAS (see figure below). At certain stages of nucleation, we transfer the surfaces contamination-free to UHV, where we analyze the chemical composition with X-ray photoelectron spectroscopy (XPS) and the atomic order of the surfaces with low energy electron diffraction (LEED) [3].

An optical anisotropy signal, which is related to the terraces at the surface, evolves during pulsed GaP nucleation at 420°C on single-domain Si(100) surfaces. This dielectric anisotropy agrees well with the one calculated for buried GaP/Si(100) interfaces from differently thick GaP eplayers. P and Si emission lines in XPS exhibit a chemically shifted second component, which quantitatively corresponds to about one monolayer and establishes simultaneously with the nucleation-related optical in situ signal. Consequently, we attribute this contribution to the existence of Si-P bonds at the buried heterointerface. Dielectric anisotropies known from atomically well-ordered GaP(100) surfaces superimpose the nucleation-related optical in situ spectra during further pulsing and annealing in phosphorus ambient. The sign of the corresponding RAS signals of the Si(100) surface before nucleation and the GaP/Si(100) surface after nucleation implies Si-P bonds at the interface [1]. These findings support a kinetically limited formation of abrupt Si-P heterointerfaces.
OMVPE GROWTH OF APD-FREE GAP ON ASH3-CLEANED VICINAL SI(100)

William E. McMahon, Emily L. Warren, Alan E. Kibbler, Ryan M. France, Andrew G. Norman, Jerry M. Olson, Adele Tamboli, Pauls Stradin

NREL, Golden, CO

Direct growth of III-V/Si enables the integration of III-V and Si optoelectronic devices for a wide variety of applications, and has therefore been the subject of much research for many decades. Most of this effort has been directed toward overcoming the two main technical challenges: 1) removing atmospheric oxygen and carbon contamination and 2) establishing the conditions needed for “APD-free” III-V epitaxy (i.e., without antiphase domains). Here we report on an OMVPE process for APD-free GaP growth on Si which overcomes these challenges by using AsH3 to clean and prepare the Si surface in situ at a relatively low temperature.

This process is based upon a very brief "AsH3-cleaning" step which simultaneously removes atmospheric contamination (thereby eliminating the need for Si regrowth) and creates a single-domain As-terminated Si surface (Fig. 1, left). This is done by heating an HF-dipped Si substrate to 780°C in a low-pressure OMVPE reactor using 0.03 Torr AsH3 diluted in 50 Torr H2 flowing at 3.5 lpm. After a few seconds at 780°C, the substrate is cooled to the growth temperature (~740°C) for 2 minutes, then GaP growth is initiated using PH3 and triethylgallium (TEG). The resulting GaP epilayers have been examined with TEM over large areas and no APDs were observed. High-resolution images of smaller areas indicate that the initial interface is also defect-free (Fig. 1, middle). LEED images show that the GaP stacking sequence follows the (Si, As, Ga, P) pattern established by the As/Si surface (Fig. 1, right).

Each step of this process has been examined using a suite of surface analysis tools, and the key process steps and fundamental epitaxial processes will be discussed in detail. Potential advantages related to performing this process in situ at a relatively low temperature will also be discussed.

Funding for this work was provided by DOE EERE through contract SETP DE-EE00025783.

Figure 1. (Left) LEED of a single-domain, double-stepped "AsH3-cleaning" As/Si(100) 4°-(111) surface with dimer rows parallel to the steps. (Middle) Cross-sectional TEM of a small region of the subsequently-grown GaP. (Right) LEED indicates that the P-P dimer rows on the GaP surface are parallel to the steps, following the template established by the As/Si surface. The box in each LEED image corresponds to a (1x1) surface unit cell.
Two dimensional (2D) transition metal dichalcogenides (TMDs) are of increasing interest for next-generation nanoelectronic and optoelectronic devices. For many applications in high volume manufacturing (HVM) of devices based on TMDs, precise control over the deposition of precursors and the corresponding deposition processes is required to achieve uniform films with monolayer control. To date, a capability for reproducible large-area, 2D TMD films with monolayer control has not been widely demonstrated. The goal of this work is to investigate potential reasons for this limitation in an effort to assist in the development of HVM TMD film deposition processes. The approach taken to achieve this goal was to focus on chemical vapor deposition of MoS₂ using a variety of precursors in a deposition system equipped with in situ diagnostics to permit precise control of the precursor flux and to characterize precursor stability and deposition chemistry. The precursors investigated in this work include (η-ethylcyclopentadienyl) dicarbonyl molybdenum, cycloheptatriene molybdenum tricarbonyl, and bis(ethylenebenzene) molybdenum for molybdenum and elemental sulfur, 1-propanethiol, propyl sulfide, and ethyl disulfide for sulfur. The precursor flux was controlled using custom-built, optical mass flow meters installed on the delivery lines while precursor chemistry was characterized in the reactor volume above the deposition surface (i.e., in the thermal boundary layer) using in situ Fourier transform infrared spectroscopy. As-deposited and annealed films were also characterized with a variety of ex situ techniques, including Raman and photoluminescence spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The use of in situ metrologies coupled with extensive ex situ film characterization, permits insight into a number of important aspects of these deposition processes, including the effect of process conditions (e.g., substrate temperature and precursor residence time) on gas-phase precursor reactions and film properties, the impact of gas-phase precursor chemistry on film properties, and the degree of control that exists for depositing different thermodynamically favored phases (e.g., by adjusting precursor stoichiometry and substrate temperature).
Transition metal dichalcogenides (TMDs) are an emerging class of layered semiconductor materials of MX2 structure (M=Mo, W, Zr etc. and X=S, Se, Te etc.) with applications for next generation nano-electronics, opto-electronics and sensors. To grow TMDs materials on a large-scale wafer, we have developed a growth reactor (Figure 1) which can be used for both chemical vapor deposition (CVD) and atomic layer epitaxy (ALE). Unlike traditional flow-tube growth method where growth take place uncontrolled fashion and also dependent on the substrates location relative to precursor-crucible, this new reactor is designed to flow precursors vertically into substrates for higher areal-uniformity and also allows an independent control of the precursors partial pressure (by varying flow-rate, bubbler temperature), growth temperature and pressure. We established a suitable chemical pathways for the growth of MoS2 films using molybdenum chloride (MoCl5) and elemental sulfur as precursors. We have demonstrated that MoS2 film can be grown by both CVD and ALE method. Through a series of experiments, we found out that the thickness of the films can be controlled and the crystalline properties of the film can be improved by selecting appropriate growth modes, substrate temperature and precursor flow rate (i.e. partial pressure). A two-step CVD growth method (A suitable high temperature growth followed by low-temperature nucleation) results in an almost fully covered substrate surface (see Figure 2). A parallel to conventional CVD growth experiments, we performed studies the pulsed feeding of precursors into the reactor to establish an ALE growth mode. The films are characterized by atomic force microscopy, reflection high-energy electron diffraction (RHEED) method, Raman spectroscopy and high resolution x-ray diffraction. A details of the growth results, alloys and heterostructure will be presented.

Figure 1. Home-built growth system for 2D materials: It can operate at ALE mode or CVD mode and the sample stage can reach temperatures as high as 1200°C.

Figure 2. Scanning electron microscopy images from the CVD and ALD grown MoS2 films on sapphire.
Vertical-cavity surface-emitting lasers (VCSELs) have numerous applications including, optical-fiber data transmission, optically pumped solid-state lasers, and chip-scale atomic clocks. The key to fabricate a conventional current-injection VCSEL largely depends on the crystal quality of distributed Bragg reflectors (DBRs) composed of epitaxially grown semiconductor materials. For the III-nitride material system, the growth of high-reflectivity DBR structures is extremely challenging due to the large lattice mismatch between GaN and AlN and the relatively low index contrast of this system. To mitigate the tensile strain originating from lattice mismatch, AlN interlayers or GaN/AlN superlattice strain management designs have been introduced for crack-free DBR growth. Aside from strain-engineered AlGaN-based DBRs, AlInN ternary alloys latticed-matched to GaN have been used for AlInN/GaN DBR growth. Other epitaxial DBR approaches included introducing boron ternary alloys as well as forming air gaps between nitride materials. Despite the great progress on developing nitride DBRs, the majority of structures demonstrated to date limit the possibility for electrical conduction due to the wide-bandgap nature of AlN. Without an electrically conducting DBR structure, lateral contacts are required, which inevitably reduce the number of devices per wafer as well as increasing fabrication complexity.

In this work, we report an electrically conducting n-type DBR consisting of 40-pairs of Si-doped Al$_{0.12}$Ga$_{0.88}$N/GaN grown in a metalorganic chemical vapor deposition (MOCVD) reactor. The Si-doped 40-pair Al$_{0.12}$Ga$_{0.88}$N/GaN DBR has peak reflectivity of 91.5% at 368 nm with a stopband of 11 nm. To study the electrical properties of the DBR, a 3 µm deep mesa etch was performed to expose the n-GaN layer below DBR. Metal contacts were evaporated on top and the bottom of 60 µm diameter circular mesas and non-linear I-V characteristics were observed. At the maximum measured current of 100 mA at ~ 7.5V, the series resistance was determined to be 20 Ω. This presentation will further discuss the material growth analysis through atomic force microscopy, X-ray diffraction, and transmission electron microscope analysis. Additional optical and electrical properties will be presented in details.
GAN/INGAN HETEROJUNCTION PHOTOTRANSISTORS GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION
Tsung-Ting Kao, Jeomoh Kim, Yi-Che Lee, Mi-Hee Ji, Sanjul Haq, Theeradetch Detchprohm, Russel Dupuis, Shyh-Chiang Shen
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III-Nitride (III-N) based photodetectors (PDs) have numerous advantages for ultra-violet (UV) radiation detection, including low dark current density, high breakdown field, and wider operational temperature range. To date, high-performance UV PDs, such as III-N p-i-n diodes, avalanche photodetectors (APDs), and metal-semiconductor-metal (MSM) detectors have been widely reported. On the other hand, phototransistors are a possible form of UV PDs that could provide high photocurrent gain through the transistor action at a biasing condition that is much lower than the device breakdown voltage. In the past, phototransistors based on lower bandgap materials have been demonstrated for effective infrared detection and for fiber-optic communications. However, since the photocurrent gain in phototransistors are also related to the epitaxial material quality of the bipolar transistor structure, very few III-N-based phototransistors were reported to date.

In this paper, we report high-performance InGaN/GaN heterojunction phototransistor (HPTs) operated under UV-light illumination. Not only can the HPTs operate in the low-voltage phototransistor mode, they can also be biased at higher voltages to enable avalanche phototransistor (APT) action. The HPT layer structure grown on (0001) sapphire consists of a 2.5-μm thick unintentionally doped GaN buffer layer, followed by a 880-nm Si-doped n-GaN sub-collector layer ($n=3\times10^{18}$ cm$^{-3}$), a 320-nm n-GaN collector layer ($n=1\times10^{18}$ cm$^{-3}$), a 30-nm In$_{0.03}$Ga$_{0.97}$N graded collector layer, a 110 nm Mg-doped In$_{0.03}$Ga$_{0.97}$N base layer ($p=1\times10^{19}$ cm$^{-3}$), a 30-nm In$_{0.03}$Ga$_{0.97}$N graded emitter layer and a 120-nm Si-doped n-GaN cap layer ($n=1\times10^{19}$ cm$^{-3}$). As shown in Fig. 1. The photoresponse spectrum shows that photons absorbed in the base layer lead to photocurrent generation, followed by a subsequent current amplification as $V_{CE}$ approaches the breakdown voltage. As shown in Fig. 2, the device performs as an HPT at low voltage region with the responsivity ($R$) of $\sim 0.5$ A/W for photons with $\lambda=373$ nm. As $V_{CE}>35$ V, photocurrent increases rapidly due to carrier multiplication, leading to significantly enhanced photocurrent gain ($h_{fe}$) and $R$. A softening of transistor breakdown characteristics was observed as the incident optical power increases. As the device biased near the avalanche breakdown region, high $R$ of $>30$ A/W and $h_{fe}$ of $>100$ are both demonstrated at $V_{CE} = 40$ V.
**Fig. 1**

- $P_{opt} = 951 \, \mu\text{W/cm}^2$
- $V_{CE} = 10 \, \text{V}$

![Diagram of a photonic device with wavelength and photocurrent values](image)
While InGaN spans all visible wavelengths, longer wavelength emitters continue to have low efficiency for reasons that are not completely understood. Several possible causes have been suggested including, 1) defects caused by lattice strain, 2) impurities incorporated at low growth temperature, and 3) larger polarization-induced electric fields, which decrease electron and hole wavefunction overlap, resulting in decreased spontaneous recombination rates. Irrespective of their source, reduction of these non-radiative recombination centers in green [1] and longer wavelength InGaN QWs is essential for nitride-based LEDs and solar cell power conversion efficiencies.

For this presentation, InGaN/AlGaN/GaN-based multiple quantum wells (MQWs) capped with AlGaN interlayers (ILs) are investigated [2], specifically to examine the fundamental mechanisms behind their increased radiative efficiency at wavelengths of 530 - 590 nm [3]. After growth of a ~3 nm thick InGaN quantum well (QW), an AlGaN IL is grown at the same temperature, followed by the growth of a ~10 nm thick GaN barrier layer at increased temperature. Capping the QW in this way with AlGaN provides various benefits. First, higher indium concentrations in the InGaN QW can be obtained by growing at a temperature well below those typically used for green QWs. Second, annealing the IL capped QW prior to the barrier growth improves the AlGaN IL smoothness, improves the InGaN/AlGaN/GaN interface quality, and increases the radiative efficiency by reducing non-radiative defects as determined by time-resolved...
photoluminescence measurements. Finally, the AlGaN IL increases the spontaneous and piezoelectric polarization induced electric fields acting on the InGaN QW, providing an additional red-shift to the emission wavelength as determined by Schrodinger-Poisson modeling and fitting to the experimental data. The relative impact of increased indium concentration and polarization fields on the radiative efficiency of MQWs with AlGaN ILs will be discussed along with implications to conventional longer wavelength emitters.

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11:30 AM - 11:50 AM
IN SITU METROLOGY DURING GROWTH OF NOVEL NITRIDE BASED SEMICONDUCTOR BRAGG MIRRORS
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Monolithically integrated DBRs are widely used to enhance light outcoupling, directionality of light output, and to narrow the emission spectra of light emitters. Such DBRs consist of periodic stacks of materials with varying refractive index. Typically, high-reflectivity mirrors require DBRs with a large number of layers as the refractive index contrast between layers is limited. Among the nitrides, lattice mismatch and distinct growth regimes for possible material combinations such as AlGaN/GaN or AlInN/GaN represent severe technological barriers to achieve highly reflecting mirrors. Moreover, tuning bandwidth and stopband position of the DBRs requires precise knowledge of growth rates over extended growth times. On-time metrology using reflectance data acquired from the growing surface provides better control of DBR growth and enables faster response to deviations during DBR evolution.

We will showcase the use of in-situ metrology for nitride DBR growth for two very attractive material combinations compatible with LED applications. One is a novel approach based on a modulation-doping scheme which provides highly-conductive, narrow-band DBRs. The other approach is based on conventional AlInN/GaN DBRs which is a lattice-matched system of high refractive index contrast. Growth of these DBRs is different and requires strategies to control the layer parameters. For the modulation-doped DBR the refractive index contrast is only about 1-2% which is obtained by high Ge-doping GaN up to 1020 cm-3. Tight control over doping levels and growth rates over 100 pairs of GaN/GaN:Ge is necessary to achieve high reflectivities at the desired wavelength. The growth of AlInN/GaN DBRs is challenging as the growth temperature for high-quality AlInN is around 800 °C whereas GaN layers are grown at 1100°C. Any deviation from the lattice-matched composition of AlInN ([In]~17%) needs to be early detected in order to avoid interface and surface roughening within the DBR.

Highly-reflecting DBRs using these materials have been successfully developed by taking advantage of latest generation in-situ metrology. We applied in-situ reflectance and curvature sensing for supporting the process development of the DBRs. Beyond standard in-situ thickness measurements of thin layers we applied newly developed fitting algorithms for precise Ge doping concentration determination already during DBR growth. A slight Ge incorporation in the nominally undoped GaN layers due to memory effects could be revealed. Lattice-matched growth of the AlInN/GaN DBR is adjusted by means of in-situ curvature sensing. AlInN growth rate measurements have been enabled by high-temperature refractive index measurements.
Quasi-phase-matching (QPM) devices based on periodically poled structure are suitable for generating the second- and third-harmonics, and ferroelectric crystals such as LiNbO$_3$ and LiTaO$_3$ are now used practically. However, they are not suitable for the UV region because of their limited optical transparency. Recently, we have realized the 350nm generation by the QPM device made of an old but novel ferroelectric crystal of LaBGeO$_5$ (LBGO). LBGO has the trigonal symmetry belonging to the space group $C_3v$. A few reports on the single crystal growth of LBGO have been reported. In order to make a QPM device, a crack-free single-domain crystal with diameter greater than 15mm required. Here, we present the Czochralski (Cz)-pulling of LBGO single crystal with good optical quality and suitable size for device fabrication. 5N purity raw materials of La$_2$O$_3$, H$_2$BO$_3$ and Ge$_2$O$_3$ were mixed in the stoichiometric ratio, and the mixture was sintered at $\sim 1100 \degree$C in air. The growth was carried out by the rf-heating Cz technique using a Pt crucible. A serious problem of significant evaporation of components during the growth has been reported. We were able to resolve this issue by growing the crystal in dry atmosphere. The pulling and rotation rates were 0.4-1.0 mm/h and 5-20 rpm, respectively. The crystal was a colorless transparency and exhibited a clear three-fold growth habit, which is a characteristic feature of LBGO. The size of crystal was 18mm in diameter with 40mm in length for the c-axis direction. The optical transmittance of c-plate was measured and the absorption edge was found to be around 195nm. From this grown crystal, periodically-poled structure was fabricated by applying conventional electric field poling method with current control. The periodicity was set around 6.4 um with multi-grating and the size of poled areas were set 15 mm in length and 5mm in width. The periodically-poled pattern with almost 50:50 duty ratio was successfully fabricated with whole device length. By using fabricated PP-LBGO device, we tested 355 nm generation by sum-frequency generation of 1064 nm and 532nm. More than 500 mW of 355 nm generation was confirmed without walk-off. In addition, PP-LBGO with much narrower periodicity (4.2 um) was also tested. By this device, 266 nm generation was confirmed from pulsed 532nm.

2:00 PM - 2:15 PM

**CONFIGURATION OF POINT DEFECTS OF IMPURITY-DOPED CONGRUENT LITHIUM NIOBATE**

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Lithium niobate (LiNbO$_3$:LN) is a ferroelectric material, and it has been used as a substrate in nonlinear optical devices. LN crystals are normally grown from a congruent melt to obtain a homogeneous composition of crystals. Since congruent LN (c-LN) contains more niobium (Nb) than stoichiometric LN, excess Nb generates intrinsic point defects in the crystal. According to the "Li site vacancy model", intrinsic defects of c-LN in the Li site are antisite Nb (Nb$_x$) and vacancies in the Li site (V$_{Li}$). In particular, Nb$_x$ causes photorefractive damage, which hinders optical application of LN. Regarding this problem, doping of impurities such as MgO is found to increase the damage resistance. However, it has not been fully understood how doping affects to the defect structure including Nb$_x$. In the present work, the defect structure and Nb$_x$ behavior of impurity-doped c-LN have been investigated by thermodynamic constraints combined with lattice constant measurements. On the basis of the "Li site vacancy model", six kinds of defect structures are possible when defect configurations in the Li and Nb sites are considered. Using thermodynamic constraints, these can be narrowed down to two kinds (structures A and B). In structure A, vacancies and Nb exist as defects in the Li site and no defects exist in the Nb site. In structure B, vacancies and Nb exist as defects in the Li site and impurities exist as defects in the Nb site. Since the relationship between impurity concentration and lattice constants for structures A and B differ, the defect structures can be differentiated by analyzing lattice constant variations as a function of impurity concentration. The results show that the defect structure of divalent and trivalent impurity-doped c-LN is structure A and that of tetravalent impurity-doped c-LN is structure B. The Nb$_x$ concentration increased with increasing tetravalent impurity concentration. In contrast, the Nb$_x$ concentration decreased with increasing divalent and trivalent impurities. The valence of an impurity determines whether the impurity is located in the Li or Nb site, consequently determining whether Nb$_x$ decreases or increases when the impurity concentration changes.


2:15 PM - 2:30 PM

**DEVELOPING PERIODICALLY ORIENTED GALLIUM NITRIDE FOR FREQUENCY CONVERSION**

Jennifer Hite$^1$, Ramasis Goswami$^1$, Jaime Freitas$^1$, Michael Mastro$^1$, Igor Vurgaftman$^1$, Jerry Meyer$^1$, Christopher Brown$^1$, Francis Kub$^1$, Steven Bowman$^1$, Charles Eddy, Jr.$^2$
$^1$US Naval Research Laboratory, Washington, DC, $^2$University Research Foundation, Greenbelt, MD

On the basis of the "Li site vacancy model", six kinds of defect structures are possible when defect configurations in the Li and Nb sites are considered. Using thermodynamic constraints, these can be narrowed down to two kinds (structures A and B). In structure A, vacancies and Nb exist as defects in the Li site and no defects exist in the Nb site. In structure B, vacancies and Nb exist as defects in the Li site and impurities exist as defects in the Nb site. Since the relationship between impurity concentration and lattice constants for structures A and B differ, the defect structures can be differentiated by analyzing lattice constant variations as a function of impurity concentration. The results show that the defect structure of divalent and trivalent impurity-doped c-LN is structure A and that of tetravalent impurity-doped c-LN is structure B. The Nb$_x$ concentration increased with increasing tetravalent impurity concentration. In contrast, the Nb$_x$ concentration decreased with increasing divalent and trivalent impurities. The valence of an impurity determines whether the impurity is located in the Li or Nb site, consequently determining whether Nb$_x$ decreases or increases when the impurity concentration changes.

Gallium nitride is a semiconductor widely used in both optical and electronic devices. The polarity of GaN (+/- c-direction) influences many properties of the resultant material, including chemical reactivity and electric field in these 'spontaneously polarized' materials. By determining their orientation, we have demonstrated control of GaN polarity on both polar faces of GaN. By employing a selective growth method to deposit the IL, the lateral polarity of the GaN can be alternated, thus enabling structures referred to as periodically oriented (PO) GaN.

On N-polar substrates, we demonstrated that optimization of the MOCVD growth rates resulted in sharp, vertical interfaces and smooth surfaces. This work has moved the technology substantially closer to practical non-linear optic emitters by using HVPE to extend the PO GaN templates on N-polar substrates to total thicknesses of up to 500 μm, while faithfully maintaining the pattern of alternating polarity. Additionally, cross-sectional cathode-luminescence (CL) imaging of such an extension shows that the large initial dislocation densities occurring in the original inversion layers greatly decreased after about 25 μm of regrowth.

For growth on Ga-polar substrates, we have demonstrated that inversion layers can be created using atomic layer deposition (ALD) of AlOx. This new capability is especially relevant because Ga-polar films are more prominent in devices, as they result in lower impurities, higher quality and smoother films. In this case, GaN grown over the inversion layer is N-polar. This inversion layer was used to form laterally-patterned stripes of alternating Ga- and N-polar films. We find that annealing the ALD films crystallizes the AlOx, thereby allowing N-polar GaN to be grown over the new sapphire-like surface. Transmission electron microscopy shows that the inversion layer in a PO GaN structure is crystalline, a-plane oriented, and α-phase. TEM characterization further indicates that the GaN layers, both above and below the AlOx inversion layer, are c-oriented without any rotation between them. The optimization of this process has enhanced the surface smoothness. The latest results in demonstrating secondary harmonic generation will be presented.

These methods of GaN polarity inversion offer the promise of engineered materials with custom lateral and vertical polarity variations for applications in novel electronic and optoelectronic devices, a subset of which are expected to be suitable for non-linear optics.

2:30 PM - 2:45 PM

IMPROVED GRATING PROPAGATION DURING HVPE GROWTH OF ORIENTATION-Patterned Gallium Arsenide

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Quasi-phase-matched semiconductors represent the future of mid-IR nonlinear optical materials, and orientation-patterned GaAs (OP-GaAs) is the first successful incarnation of this technology. GaAs offers very high nonlinearity (d33=94 pm/V) and thermal conductivity (55W/mK), and when grown from the vapor phase exhibits extremely low 2-μm absorption losses (< 0.01 cm⁻¹). The application of OP-GaAs has been limited by the availability of samples with sufficient thickness, grating quality, and transparency for practical device applications. This limitation has been overcome by advances in all-epitaxial growth of OP-GaAs, by which polar-on-nonpolar MBE is used to grow epitaxial GaAs on a thin Ge buffer layer with an orientation that is inverted with respect to the GaAs substrate. The inverted layer is photo-lithographically patterned and etched with the desired grating structure, and alternating orientations are then re-grown first by MBE followed by hydride vapor phase epitaxy (HVPE) at rates up to 200 μm/hr to produce thick QPM layers for in-plane laser pumping. A significant limitation to scaling OP-GaAs to larger apertures (i.e., greater thicknesses) has been the tapering of domain wall boundaries: instead of parallel vertical propagation of both polarities, it is observed that domains nucleating on the original (etched) substrate orientation grow gradually wider at the expense of the adjacent domains growing on the inverted layer. As a result the duty cycle of the MBE template gradually shifts away from the optimal 50:50 (degrading conversion efficiency) until ultimately the inverted domains are annihilated. Previous work has shown that the domain spreading angle can be minimized by growth at lower temperatures (680°C), but we have achieved better material quality and OPO performance for growth closer to 710°C at the expense of worse domain spreading. In parallel work on orientation-patterned gallium phosphide (OP-GaP) we observed near-perfect domain propagation at elevated growth temperatures (795°C) and V/I ratios > 6. In this work we examined the effect of V/I ratios ranging from 3 (typical) to nearly 6 on domain propagation at 710°C, but the domain spreading was unaffected by the V/I ratio. Instead, lower growth rates (60 compared to more typical 130 μm/hr) significantly improved grating propagation. In the past it was difficult to propagate grating periods much below 50 microns, but at reduced HVPE growth rates we have demonstrated parallel grating propagation in OP-GaAs at grating periods as low as 8.7 microns (i.e., 4.35 micron domain widths).

2:45 PM - 3:00 PM

POLARIZATION DEPENDENCE OF SECOND HARMONIC GENERATION IN CUBIC CRYSTALS

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With the advancement of orientation patterning technology which allows (quasi) phase matching to take place over many centimeters of path length, semiconductors with cubic crystalline symmetry such as GaAs and GaP, with high values of nonlinear optical coefficient, have become leading candidates for frequency conversion of laser beams. For an optical parametric oscillator (OPO) on GaAs, Vodopyanov et al. observed the relative polarization directions of the pump, signal and idler beams [1]. A detailed treatment of the relative polarization directions of pump and generated beam is not easily available for the case of second harmonic generation (SHG) in GaAs, although Oron et al observed that with pump polarization along the face diagonal (111) the generated polarization is also along the same direction (111). With pump polarization along the face diagonal, the SHG polarization is also along the same direction (111). With pump polarization along the body diagonal (111) no SHG is generated. Calculations explaining these observations will be presented.

References:
Quantum Cascade Laser Active Regions on Metamorphic Buffer Layers
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We describe the use of Metamorphic Buffer Layers (MBLs) as substrates with variable lattice constant for designing and fabricating intersubband transition sources involving strained superlattices (SLs) such as Quantum Cascade Lasers (QCLs). Thick (10-18 μm) compositionally-graded, hydride-vapor-phase epitaxy (HVPE)-grown MBL structures are employed as substrates. The buffer structure encourages the formation of misfit dislocations as a means to relieve film stress without generating threading dislocations. We previously reported the use of Chemical-Mechanical-Polishing (CMP) followed by wet-chemical etching to improve the surface morphology of MBLs, while maintaining an epi-appropriate surface chemical composition and structure [1].

To accommodate the large electron-transition energies for short-wavelength QCLs, deeper wells and taller barriers (i.e., higher strain) are necessary to prevent excessive active-region carrier leakage. These layers are limited by strain-thickness considerations in order to avoid strain relaxation. We have designed and grown short-wavelength QCL structures with low strain (Δa/a~1.6 %) on MBLs with a lattice constant intermediate between that of GaAs and InP (In0.22Ga0.78As). The design employs single-phonon-resonance (SPR) depopulation scheme such that states 2 and 1 in lower laser level of active region are separated by at least the energy of one phonon (i.e., 34 meV). The emission wavelength is calculated to be 3.40 μm.

Strained-layer 20-period InxGa1-xAs (wells)/AlyIn1-yAs (barriers) SL test structures and 10-period QCL active regions are grown by OMVPE on polished MBLs. The HVPE-as-grown layers displayed some pits and crosshatching. Peak-to-valley crosshatching is as high as 100 nm on an as-grown MBL, measured using a Zygo white-light interferometer. Atomic force microscopy (AFM) measurements indicate that the rms surface roughness of the MBL can be reduced from 3.67 nm for as-grown structures to 1.34 nm post CMP; also reducing the crosshatching. A brief wet-chemical etch removes residual damage, from the surface, introduced by CMP. High-resolution X-ray diffraction (004) and (115) Reciprocal Space Maps (RSM) were measured to determine the lattice constant and relaxation percentage of the MBL and characterize the SL films grown atop the MBL. The RSM projection on Omega2Theta axis in (004) direction for the 10-period QCL active region atop the MBL is shown in attached figure.

The use of an MBL allows for accessing a compositional range of materials which would otherwise be prohibited due to excessive strain on conventional substrates; thus, finding application in realizing short-emission-wavelength QCL of potentially significantly improved performance.

feature that may make possible high-performance heterostructures. The availability of lattice matched sacrificial layers, such as AlAs, and selective wet-chemical etches expands the range of applications to include free-standing nanomembrane (NM) single- or multilayer structures that can be transferred to new hosts. Thus we have earlier shown that Ge can be strained in such a manner as to overcome the indirect nature of its fundamental energy bandgap. We expect to be able to fabricate higher-quality Ge NMs using GaAs as a substrate, thus expanding the range of achievable strains. Possible initial applications include tunable Ge LEDs composed of epitaxially grown Ge P-I-N junctions and GaAs/Ge/GaAs heterostructures that exhibit topologically insulating behavior [1]. AlAs/GaAs bilayers grown on a GaAs(001) substrate and subsequently released using selective-etch procedures have been demonstrated. The addition of a Ge layer completes the desired AlAs/GaAs/Ge NM heterostructure. We show initial results of growth, release, and characterization of GaAs and GaAs/Ge/GaAs trilayer NMs and their transfer and bonding to different host substrates.


Supported by MRSEC and DOE

2:10 PM - 2:30 PM

**INP-BASED METAMORPHIC HIGH INDIUM INALAS/INGAAS EPITAXIAL STRUCTURES FOR LASERS AND DETECTORS IN 2-3μM RANGE**

Yi Gu, Y. G. Zhang, X. Y. Chen, S. P. Xi, B. Du, Y. J. Ma, L. Zhou
Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, China

The semiconductor lasers and detectors in short wave infrared of 1-3 μm, especially the longer 2-3 μm range, have attracted much attention due to the unique spectral features in this band and extensive applications in gas monitoring, bio-molecules detection, remote sensing, etc. There are several material systems for the developments of lasers and detectors in this wavelength range. In III-V semiconductors, antimonides lattice-matched to GaSb substrate can cover this wavelength range, however, the difficulties in the treatment of Sb-containing materials still exist in both epitaxy and processing aspects. In addition to antimonides, InP-based InAlGaAs is a more mature III-V material system with widely adjustable lattice constant and bandgap, and InP substrate with high quality is more available than GaSb. For the In0.52Al0.48As/In0.53Ga0.47As heterstructures lattice-matched to InP, the luminescence and absorption wavelengths from interband transition are limited shorter than 1.7 μm, where InGaAs is used as the active material and InAlAs as the barrier material. Increasing the indium composition can extend the wavelengths to the 2-3 μm range, however, induces InxAl1-xAs/InxGa1-xAs materials no longer lattice-match to InP substrate. The material quality becomes the crucial problem in these metamorphic lasers and detector structures.
In this presentation, we will present our recent works on the development of InP-based high quality metamorphic high indium InAlAs buffer as well as the following demonstration of high indium InGaAs/InAs quantum well lasers and InGaAs detectors on the metamorphic buffer. The growth temperatures and grading profiles of the buffer were optimized in detail and the indium composition overshoot was introduced. InGaAs/InAs quantum well laser structures were grown on InP-based metamorphic In0.8A0.2As template. Considering the limited material choices, the barrier and waveguide layers were optimized carefully. By using this metamorphic scheme, lasers with lasing wavelength beyond 2.5 μm were demonstrated and the longest lasing wavelength arrived at 2.9 μm. In addition, by using the pseudomorphic scheme, quantum well lasers in 2.0-2.4 μm range were demonstrated. Therefore, InP-based quantum well lasers in 2-3 μm range have been developed. By using various indium compositions from 0.6 to 0.9, a series of the InxGa1-xAs detectors with the cutoff wavelength from 1.7 μm to 2.9 μm were grown and demonstrated. The InGaAs/InAs superlattice electron barrier was inserted in the absorption layer to suppress the dark current but keep the nearly unchanged optical current.
In this study, the HPCVD growth of Bi$_2$Se$_3$ oriented films were obtained at a substrate and Se temperature of 220°C and 350°C, respectively. At the cracking temperature of 350°C, the increase in substrate and Se cracking temperature was varied from 290°C (1.6x10$^{19}$ cm$^{-3}$) to 350°C (8.4x10$^{19}$ cm$^{-3}$), but subsequently the carrier concentration increased as the pre-cracking temperature was raised to 540°C (1.5x10$^{19}$ cm$^{-3}$). At the pre-cracking temperature of 350°C the increase in substrate and Se cracking temperature was raised to 540°C (1.5x10$^{19}$ cm$^{-3}$). The effects of substrate and pre-cracking temperature on the structural and electrical properties of the Bi$_2$Se$_3$ films were investigated. C-axis oriented films were obtained at a substrate and Se temperature of 220°C when the pre-cracking temperature was varied from 290-540°C. Room temperature Hall-effect measurements showed a reduction in the carrier concentration as pre-cracking temperature was increased from 290°C (1.6x10$^{19}$ cm$^{-3}$) to 350°C (8.4x10$^{19}$ cm$^{-3}$), but subsequently the carrier concentration increased as the pre-cracking temperature was raised to 540°C (1.5x10$^{19}$ cm$^{-3}$). The effects of substrate and pre-cracking temperature on the structural and electrical properties of the Bi$_2$Se$_3$ films were investigated. C-axis oriented films were obtained at a substrate and Se temperature of 220°C when the pre-cracking temperature was varied from 290-540°C. Room temperature Hall-effect measurements showed a reduction in the carrier concentration as pre-cracking temperature was increased from 290°C (1.6x10$^{19}$ cm$^{-3}$) to 350°C (8.4x10$^{19}$ cm$^{-3}$), but subsequently the carrier concentration increased as the pre-cracking temperature was raised to 540°C (1.5x10$^{19}$ cm$^{-3}$).
In this talk, I will discuss our recent work in introducing black phosphorus (BP) to the layered-material family as a novel anisotropic 2D material for electronic and optoelectronic applications. Narrow gap BP thin film (0.3 eV in bulk) serendipitously fill the energy space between zero-gap graphene and large-gap TMDCs, making it an promising material for near and mid-infrared optoelectronics. BP thin films show high mobility above 650 cm²/V.s at room temperature along the light effective mass (x) direction, implying its promising potential for high frequency, thin-film electronics. Furthermore, its anisotropic nature within the plane of the layers may allow for the realization of conceptually new electronic and photonic devices impossible in other 2D materials. In the talk, I will also present our work in demonstrating 20 GHz black phosphorus radio-frequency transistors. Our recent progress in characterizing the optical properties of single-layer black phosphorus will be discussed. I will conclude with remarks on promising future directions of black phosphorus research and how this new material is expected to benefit the next-generation electronics and photonics technologies.

SURFACE STRUCTURE DETERMINATION OF TWO-DIMENSIONAL NICKEL SILICIDE (Ni2Si) ON Ni(111) BY LEED

Md. Sazzadur Rahman, Takeshi Nakagawa, Seigi Mizuno
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The consequences of the researches on ultra-thin film formation has been progressed significantly for the last decade. Most of the efforts on the ultra-thin film technology have primarily been concentrated on growth of the two-dimensional (2-D) layer because of the different properties of the 2-D layers from those of the bulk.

In order to study on the Schottky barrier formation, the surface alloys by metal on semiconductor (M/S) have been reported vastly, but in paradox not much number of reports are found for the reverse systems, semiconductor on metal (S/M). One of the typical example of (S/M) system is Si-Ni system. Lalmi et al. reported formation of 2-D silicide for this system, but they did not study the structure model of the silicide [1]. In this work, we aimed to determine the surface structure of the formed silicide on Ni(111). Experiments were performed in an ultrahigh-vacuum chamber equipped with a four-grid LEED and AES measurement system. A Ni(111) substrate was cleaned via several cycles of Ar-ion sputtering and subsequent annealing at 1050 K for 7 min until a sharp p(1×1) LEED pattern was obtained. The deposition of Si was carried out by direct heating of a piece of Si wafer. A charge-coupled device camera with a computer-controlled data acquisition system was deployed to measure the LEED spots intensities. A Barbieri-Van Hove symmetrized automated tensor LEED package was used to determine the atomic positions [2]. The automated search algorithm was guided by the Pendry’s reliability factor. Auger electron spectroscopy was used to elemental detection and to determine the Si-coverage.

In this work, we observed the phase transition for Si-adsorption on Ni(111) as a function of Si-coverage. Figure 1 (a) and (b) represent the obtained LEED patterns of (3\*3)R 30° and (2\*2) phases. The (3\*3)R 30° phase has been reported earlier [1], but the (2\*2) phase is observed for the first time for Si-adsorption on Ni(111). Though the (3\*3)R 30° phase was observed previously, but the atomic positions were not determined yet. In this work, we have determined the atomic structure of the (3\*3)R 30° phase.
with chemical composition of (Ni2Si). The top views of the surface structural model of ($\sqrt{3}$×$\sqrt{3}$)R 30° phase is presented in fig. 1 (c). We also have the aim to determine the surface structure of the (2×2) phase. One of the tentative surface structure model (top view) of (2×2) phase is shown in fig. 1(d).

References:


1:30 PM - 1:50 PM

III-NITRIDE GROWTH BY A NEW GENERATION OF MBE SYSTEMS

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A new generation of high growth rate (greater than 8 um/hour) MBE systems has led to a significant advance in the growth of III-Nitrides. While MBE has long been shown capable of growing non-phase-separated InGaN materials throughout the composition range, practical thicknesses for commercial devices have been elusive due to low growth rates of ~0.2-0.4 um/hr - until now. Growth of pseudo-bulk substrates (several ums) of various III-Nitride alloys ranging from AlN to GaN to InN will be detailed. Difficulties due to limited Al flux significantly limits the growth rate of AlGaN alloys to <1 um/hour while all alloys of InGaN can be grown at significantly faster rates up to 8 um/hr. Crystal quality and surface flatness is maintained at 0.8 nm rms with clear step flow growth demonstrated via AFM (see figure 1). Structural quality is comparable to traditional multi-micron MOCVD templates (X-ray rocking curves with ~300 arc-sec) for growth up to about 5 um/hr with a slight drop off in quality beyond that rate. Thin and thick films have been grown with significant attention devoted to InGaN compositions within the solar relevant range (In~10-50%) and in the green light emitter range. It will be shown via TEM that significant improvement in the structural quality, both reduced stacking fault density and significant reduction in the threading dislocation density, can be demonstrated at low growth temperature (350-500 degrees C) with excellent uniformity (<2% over a 2 inch wafer). A significant challenge from traditional silicon doping was encountered requiring the replacement of Silicon by Germanium as an n-type dopant. P-type doping has achieved similar results as previous lower growth rate metal modulated epitaxy efforts with hole concentrations in excess of 10^{19} cm^{-3} demonstrated. This growth technique has previously led to hole concentrations as high as 7.9x10^{19} cm^{-3} and activation efficiencies in excess of 50% in p-type GaN exhibiting minimal carrier freeze-out with a resistivity less than 0.3 ohm-cm at room temperature and <1 ohm-cm even at 80K which is attributed to impurity band conduction. [1] B. Gunning, J. Lowder, M. Moseley and W. A. Doolittle, Appl. Phys. Lett., 101, 082106 (2012).


1:50 PM - 2:10 PM

MATERIALS CHALLENGES FOR HIGH-VOLTAGE SiC POWER DEVICES

D. Kurt Gaskill, Rachael L. Myers-Ward, Paul B. Klein, Kevin M. Daniels, Anthony K. Boyd, Nadeem A. Mahadik, Robert E. Stahlbush
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Silicon carbide (SiC) is a material of great interest for high-temperature, high-voltage and high-power switching device applications. Key materials challenges inhibiting such devices include elimination of basal plane dislocations (BPDs) and the enhancement of minority carrier lifetimes in the drift or blocking regions of the device. Recent progress in addressing these issues is presented. BPDs are a major concern for the SiC bipolar devices required for high-voltage applications as they source Shockley type stacking faults when exposed to electron-hole plasma and reduce minority carrier lifetimes near the defects. Many approaches have been investigated to reduce the BPD density including variation of pre-growth treatments, substrate orientation, growth parameters and growth interrupts. Previously we showed that the conversion of BPDs to threading edge dislocations (TEDs) continues throughout
the epitaxial growth process in 4° off-axis SiC material and that a minimum thickness of ~16 μm is required to convert all BPDs to TEDs. In this work we show that optimizing a hydrogen etch of the substrate prior to epitaxial growth significantly enhances conversion efficiency in a thin highly doped n+ buffer layer (BL). For these results, the epitaxial layers were grown on 4° off-axis substrates in an Aixtron/Epigress VP508 horizontal hot-wall reactor using the standard chemistry of silane (2% in H2) and propane at reduced pressure and the BPD density was mapped by using uv photoluminescence spectroscopy. In addition, lateral variations in minority carrier lifetime are also undesirable as it causes variations in the performance of switches utilizing PiN structures. Measured variations can result from three possible origins: (1) nonuniform surface recombination velocity, (2) nonuniform trap density in the epitaxial layer and (3) nonuniform interface recombination rate. We give illustrative examples of the lifetime variations that have been observed. Preliminary deep level transient spectroscopy results on a single wafer suggest that the trap density variation in the thick epitaxial layer is insufficient to produce the observed lifetime variations, implying recombination effects at the surface and/or the substrate interface are dominating the nonuniform sample response. Measurements of lifetime inhomogeneity in additional samples are ongoing in order to determine whether these results apply generally or are specific to the wafer in question. This work is supported by the Office of Naval Research.

2:10 PM - 2:30 PM

IN SITU STRESS MEASUREMENTS DURING DIRECT MOCVD GROWTH OF GAN ON SiC

Zakaria Y. Al Balushi, Joan M. Redwing
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The growth of GaN by metalorganic chemical vapor deposition (MOCVD) is of interest for power electronics used to develop efficient high power modules and inverters for hybrid and electric vehicles (HEVs). However, GaN-based power electronics are primarily lateral structures, which suffer from high on-resistance and current collapse. Vertically conducting GaN-based power devices are effective in suppressing current collapse and achieving much higher power densities. The development of GaN-based vertical devices has been limited due to the absence of viable substrates beyond bulk GaN. Vertical GaN-on-SiC devices can be an alternative to GaN-on-GaN for power electronics. The heteroepitaxial growth of GaN on SiC is challenging due to the large lattice mismatch and poor wetting behavior of Ga on the surface of SiC. In addition, the thermal expansion mismatch can lead to large stress and film cracking during cooling. Although AlN is commonly used as a buffer-layer for the epitaxy of GaN-on-SiC, it introduces a barrier at the interface, inhibiting current flow. Despite these challenges, high-quality buffer-free growth of GaN-on-SiC has been achieved, however, there are limited studies on understanding the evolution of film stress in this growth process. In situ curvature measurements were utilized to monitor the growth stress of thick (>2.5µm) GaN films grown on (0001) 6H-SiC by MOCVD. For the direct growth of GaN on SiC, a two-step temperature growth process was utilized. The two-step GaN consisted of an initial low-temperature layer grown at 900°C and a main high-temperature GaN layer grown at 1100°C. Additionally, high-temperature growth of GaN was also carried with an AlN buffer-layer on SiC. With the AlN buffer-layer, GaN grew under an initial compressive stress of -1.036GPa which gradually relaxed with thickness to -0.170GPa. In the case of GaN grown directly on SiC, the high-temperature GaN grew initially under compressive stress (-0.345GPa) which evolved into tensile stress (0.274GPa) above 300nm. Weak-beam TEM showed predominate (a+c)-type dislocations in both cases. An improvement in the surface roughness of GaN was observed for the direct growth of GaN-on-SiC (RMS=1.44nm) in comparison to the growth with an AlN buffer-layer (RMS=4.09nm). However, cracking of the GaN film was observed when AlN was not utilized. Utilizing a combination of in situ curvature measurements and ex-situ characterization, the effect of the initial GaN layer temperature and the introduction of low Al content AlGaN was investigated in the attempt to mitigate stress and cracking of the GaN films grown directly on SiC.
GaN growth on silicon in the recent past has found enhanced interest in power and optoelectronics for its cost effectiveness and potential advantage of growth on large areas. However, growth on silicon comes with its own challenges. Excessive wafer bow, film cracking, poor morphology, and wafer breakage are common issues that have to be overcome. In addition the stringent leakage specifications of \(< 1-10 \mu A/mm^2\) at 600V up to 150°C, \(< +/\sim 50 \mu m\) in bow, and the requirement of gold free processing for CMOS compatibility, makes the development of GaN/Si epitaxy a significant challenge.

In this presentation, the development of crack free, pit free, high voltage dispersion free buffers on 200mm silicon substrates overcoming the aforementioned challenges will be presented. By utilizing step graded buffers with low temperature AlN interlayers, AlN/AIGaN superlattice buffers, and carbon doping of the buffers, symmetric buffer leakage of \(< 1 \mu A/mm^2\) up to 500V at room temperature and up to 280V at 150°C has been achieved – thus qualifying the buffers for the 200V platform. A hypothesis to explain the improvement in buffer leakage characteristics due to carbon doping will be given. Initial demonstration of enhancement mode operation of HEMT devices grown on these buffer layers will also be presented.

The challenges to be overcome to improve the leakage characteristics to \(< 1 \mu A/mm^2\) at 600V or more at 150°C, trap characterization to understand the issue behind the leakage and current collapse, open questions regarding leakage mechanism and limitations will also be discussed.

\[ 150^\circ C \]

Fig. 1: Buffer leakage characteristics of the step-graded buffer stack with LT-AlN interlayer, showing the buffer leakage characteristics at room temperature (left) and at 150°C (right).
Fig. 2: Buffer leakage characteristic of the buffer stack with an AlN/AlGaN super-lattice structure, showing the leakage characteristics at room temperature (left) and at 150°C (right).

Fig. 3: Dispersion characteristics of LT-AlN interlayer buffer (left) and superlattice buffer (right) at 25 and 150°C.
Tuesday, August 4, 2015
3:30 PM - 5:00 PM
Materials for Photovoltaics and Energy Technology (Joint ACCGE/OMVPE) 1

Location: Gallatin
Session Chair(s): Ted Ciszek, Aleksandar Ostrogorsky

3:30 PM - 3:50 PM
PARTICLE ENGULFMENT DYNAMICS DURING THE GROWTH OF CRYSTALLINE SILICON
Yutao Tao, Andrew Yeckel, Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

A major challenge for the growth of multi-crystalline silicon is the formation of carbide and nitride precipitates in the melt that are engulfed by the solidification front to form inclusions. These lower cell efficiency and can lead to wafer breakage and sawing defects. Minimizing the number of these engulfed particles will promote lower cost and higher quality silicon and will advance progress in commercial solar cell production.

To better understand the physical mechanisms responsible for such inclusions during crystal growth, we have developed finite-element, moving-boundary analyses to assess particle dynamics during engulfment via solidification fronts. Two-dimensional, steady-state and dynamic models are developed using the Galerkin finite element method and elliptic mesh generation techniques in an arbitrary Eulerian-Lagrangian (ALE) implementation. This numerical approach allows for an accurate representation of forces and dynamics previously inaccessible by approaches using analytical approximations.

An example result is shown in the figure, where a SiC particle is engulfed by solidifying silicon. We consider realistic properties representing heat transfer, flow, segregation, solidification, and particle dynamics. The representation of interfacial phenomena is particularly important, and the model accounts for pre-melting effects and disjoining forces arising from van der Waals interactions, Gibbs-Thomson curvature effects, and constitutional effects on melting temperature.

We discuss significant nonlinear phenomena in this system and emphasize outcomes that have not been revealed by prior idealized approaches. Of particular interest and relevance is the discovery that oscillating solidification fronts, as would arise due to turbulent fluctuations in large-scale silicon melts, can drive engulfment of silicon carbide particles at average growth rates far below those predicted by prior steady-state analyses. This heretofore unexamined mechanism may provide an explanation for the inability of classical, steady-state analyses to describe engulfment conditions in realistic growth systems.

Figure: Computation of a SiC particle engulfed by solidifying silicon. (a) Snapshot of finite element mesh used in this calculation, with particle and solidification front indicated in red. (b) System geometry, with solute concentration field (left) and temperature contours (right). A thin, premelted liquid layer, on the order of nanometers in thickness, always separates the particle from the crystal and is accurately resolved by our model.

This research was supported in part by the U.S. National Aeronautics and Space Administration, NNX10AR70G, the content of which does not necessarily reflect the position or policy of the United States Government, and no official endorsement should be inferred.

3:50 PM - 4:10 PM
DYNAMICS OF HORIZONTAL RIBBON GROWTH OF CRYSTALLINE SILICON
Mia Divecha, Andrew Yeckel, Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

Horizontal ribbon growth (HRG) may allow the growth of crystalline silicon orders of magnitude faster than vertical ribbon growth technologies. If successful, this process would enable the production of higher-quality, near-single-crystalline silicon wafers at a fraction of the cost of current production techniques. Bleil successfully grew single-crystal germanium ribbons in the late 1960's. Large-scale development efforts for photovoltaic silicon growth were subsequently carried out by Kudo in Japan in the late 1970's and by the Energy Materials Corporation in the US in the early 1980's. However, after encouraging early results, experimental
advances and process development efforts stalled, and this technique was abandoned in favor of vertical EFG methods that were easier to develop.

We present a comprehensive thermal-capillary model based on finite-element methods to study the coupled phenomena of heat transfer, melt flow, segregation, and interfacial phenomena during the growth of crystalline silicon via the HRG process. The figure below shows a schematic representation of the HRG process and model.

Bifurcation analysis coupled with transient computations using this model reveal process limitations consistent with failure modes that have been observed in prior experiments of Kudo. Of particular interest are phenomena that control the solidification of the leading edge of the crystal ribbon. Our heat transfer models predict undercooling to occur in the melt in front of the leading edge at high growth rates. In addition, experimental development of a similar process, the Floating Silicon Method at Applied Materials, has identified the formation of a (111) facet along this leading edge, with associated melt undercooling. Dendritic instabilities arise from undercooling at this growth front and limit the achievable steady growth rate of the ribbon.

We describe our attempts to analyze the stability and dynamics of this leading edge by applying a growth kinetic law that allows for facet formation and melt undercooling within our existing thermal-capillary model. Understanding the physical underpinnings of this leading-edge instability may point the way to delaying the onset of dendrite formation and achieving substantially higher growth rates.

Figure: A thermal-capillary finite element model is applied to understand continuum phenomena during the horizontal ribbon growth of crystalline silicon sheets.

This research was supported in part by the U.S. National Science Foundation, CBET-1336164, the content of which does not necessarily reflect the position or policy of the United States Government, and no official endorsement should be inferred.

4:10 PM - 4:30 PM
NUMERICAL STUDY OF IMPURITY TRANSPORT IN CZOCHRALSKI SILICON MELT DURING HEAVILY ARSENIC-DOPED SILICON CRYSTAL GROWTH
Thi Hoai Thu Nguyen, Jyh-Chen Chen, Chun-Hung Chen, Huy Bich Nguyen
1National Central University, Taoyuan, Taiwan, 2Sino-American Silicon Products Inc., Hsinchu, Taiwan, 3Nong Lam University, Ho Chi Minh, Viet Nam

An investigation of the impurity transport in the silicon melt during heavily doped crystal growth with arsenic has been carried out numerically. The effects of arsenic evaporation from the melt-free surface and its incorporation into the ingot are taken into account by using quasi-steady modeling. The simulation results have shown that the oxygen concentration along the crystallization interface for higher crystal length lessens due to the reduction in thermodynamic oxygen activity coefficient in melt and the segregation coefficient of oxygen at the interface. In heavily doped silicon melt with arsenic, oxygen segregation coefficient is less than unity and decreases with increasing dopant content in the melt. Otherwise, there is a decrease in crystal resistivity at the higher fraction of solidified molten silicon. An inverse relationship between crystal resistivity and arsenic content is also clarified. The simulated results are in good agreement with the experimental ones as well as the results from the previous literatures.

4:30 PM - 4:50 PM
CONTROLLED FACETING AND MORPHOLOGY FOR OPTIMIZED LIGHT-TRAPPING IN ALUMINUM-CATALYZED SILICON NANOSTRUCTURES
Mel F. Hainey, Jr., Chen Chen, Marcie Black, Joan Redwing
1Penn State University, University Park, PA, 2Advanced Silicon Group, Lincoln, MA

Silicon nanowire and nanopyramid arrays fabricated using vapor-liquid-solid (VLS) growth are promising light-trapping structures for photovoltaic applications. However, to maximize light trapping, the sidewall geometry and faceting of the nanostructures must be controlled. Previous reports have demonstrated control of sidewall tapering of silicon nanowires using gold-catalyzed VLS growth, but since gold acts as a mid-level trap in silicon, it is not a suitable catalyst metal for electronic or photovoltaic applications where...
long minority carrier lifetimes are desirable. Aluminum on the other hand is a dopant in silicon and is not as effective as a recombination center. In this report, we demonstrate controlled tapering and sidewall faceting in aluminum-catalyzed nanowire growth, leading to the fabrication of low-reflectivity nanopyramid arrays.

The nanowire geometry was controlled by changing the nanowire growth temperature, which in turn affects the sidewall structure and tapering. The substrates used for growth consisted of a 10 nm Al film deposited on (111) Si. VLS growth was performed in a hot wall chemical vapor deposition reactor using SiH4 as the source gas in a hydrogen ambient. A 700oC pre-anneal at roughly 3 Torr was performed before changing to the final growth temperature and initiating growth at 500 Torr. At a 650C growth temperature, VLS growth produced six-sided vertical nanowires with minimal tapering. However, as the growth temperature increased to 675oC and 700oC, the wire sidewalls changed from six-sided to three-sided and the wires tapered to a pyramidal structure. The degree of tapering increased with increasing growth temperature. Base diameters are wider at higher temperatures as a result of increased Ostwald ripening, which promotes the formation of larger catalyst droplets. Tapering is also increased at higher growth temperatures, as the increased temperatures promote greater aluminum diffusion away from the catalyst droplet during growth. Control of nanowire tapering subsequently allows for the fabrication of low-reflectivity nanowire or nanopyramid arrays. As nanowire tapering increases and the structures shift from nanowires to nanopyramids, the reflectivity decreases across the visible spectrum, with reflectivities of 4% or less from 600-800nm for pyramidal structures, and reflectivities less than 10% over the range from 300-800 nm for pyramids grown at 700C. These structures can be fabricated in large area arrays, and serve as promising light-trapping structures for direct integration into photovoltaic devices.

Figure 1 – Aluminum-catalyzed nanowires grown at [a,e] 650C (b,f) 675C, and (c,g) 700C – showing the transition from hexagonal to triangular sidewall structure with increasing temperature. d) Reflectivity measurements show how the transition to a more tapered structure leads to reduced reflectivities across the visible spectrum.
Nonlinear Optical and Laser Host Materials (ACCGE) 2

Location: Madison
Session Chair(s): Dave Zeimon

3:45 PM - 4:00 PM
MATERIAL ASPECTS OF THE NONLINEAR FREQUENCY CONVERSION IN OPGaP AND OTHER RELATED QPM MEDIA
Vladimir L. Tassev1, Shiva Vangala1, Michael Snure1, Martin Kimani1, Rita Peterson1
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Frequency conversion in orientation patterned (OP) materials is a leading approach for generating tunable mid- and longwave IR radiation for a wide variety of military and commercial applications in defense, security, industry, science and medicine. Due to the strong interest in this matter, a number of nonlinear optical materials are currently at different stages of intensive investigation. Due to its unique properties, such as low two-photon absorption (2PA) in the convenient pumping range 1-1.7 μm and high thermal conductivity, GaP is one of the most promising nonlinear optical materials. However, some difficulties related to the low quality of the available GaP wafers and the parasitic nucleation that reduces the growth rate and deteriorates the layer quality in growth experiments longer than 4 hours indicated that OPGaP will be another battle on the scientific field. The efforts, described in this work, give some details about how using an original approach > 300 μm thick high quality OPGaP with excellent domain fidelity can be repeatedly grown in one-step HVPE growth process. Growth rates of more than a 100 μm/h on two different types of OPGaP templates, wafer bonded and with MBE assisted polarity alternation, have been achieved. AFM, SEM, XRD, EDS and TEM revealed smooth surface morphology, abrupt interfaces between the substrate and the grown material and high crystalline quality. Specific optical characterizations confirmed: (i) minimized IR absorption in the range 2-4 μm, where a persistent absorption band attributed to free carriers typically exists in all n-type commercially available GaP samples, (ii) low 2PA (ï≥0.1 cm/GW, compare with 15-16 cm/GW for GaAs) in the wavelength range of interest, and (iii) low optical loses. Second harmonic generation and nonlinear frequency conversion in the IR region are in the way to be confirmed. Other related nonlinear materials, such as GaN and ZnSe, have been also explored for their feasibility for frequency conversion in the IR and THz region. New growth approaches and template preparation techniques have been applied. Some crystallographic considerations on: (i) the appearance during the deposition of the (111)b terminated facet that could trigger the overgrowth of the template pattern, and (ii) how alternating the polarity may favorably affect the growth near the interface between the substrate and the growing HVPE layer are also provided.

4:00 PM - 4:15 PM
ALL-EPITAXIAL GROWTH OF DEVICE-QUALITY ORIENTATION-PATTERNED GALLIUM PHOSPHIDE FOR MID-INFRARED OPTICAL PARAMETRIC OSCILLATORS
Peter G. Schunemann, Daniel J. Magarrell, Leonard A. Pomeranz
BAE Systems, Nashua, NH

Orientation patterned gallium phosphide (OP-GaP) is a new nonlinear optical (NLO) crystal which exhibits the highest nonlinear coefficient (d14=70.6 pm/V) and the longest infrared cut-off (12.5 μm) of any quasi-phase-matched (QPM) material that can be pumped with widely-available 1-μm lasers.

QPM structures are first grown by polar-on-nonnorl MBE on 3-inch (100) GaP substrates (4° off cut toward ). A 200-μm-thick buffer is grown at a rate of 200 nm/h under a P pressure of 1.1×10^-6 torr at 500°C followed by 5 nm of Si at a rate of 15 nm/h while ramping from 380°C to 450°C. A 2.7-μm-thick AlGaP smoothing layer and then a 100-μm-thick inverted GaP layer are grown at 200 μm/hr at P pressures of 3.3 x 10^-7 torr and 4.3 x 10^-7 torr respectively. The GaP inverted layer is then lithographically patterned with grating periods ranging from 14.5 to 95.9 μm and then reactive-ion etched in BC13 at rates of ~ 2 μm/s (0.4 nm/s for Si) down to the surface of the original substrate. The photoresist is stripped, the wafer is cleaned, and 200 μm of GaP are regrown under the same conditions as the initial GaP buffer layer.

The thickness of the MBE-grown templates is extended to > 500 microns by hydride vapor phase epitaxy in an AIXTRON 103 LP-VPE reactor according to the reaction GaCl + PH3 -> GaP + H2 + HCl. Initial experiments performed at a 726°C and V/III ratios of 2.2 yielded 164 microns of growth in 2 hrs with poor epitaxial quality and rapid self-annihilation of periodic domains structures. Subsequent experiments on unpatterned GaP wafers at higher growth temperatures yielded better epitaxial quality (rocking curve FWHM = 24 arc sec) but exhibited a high density of elongated hexagonal surface pits which were ultimately eliminated by increasing the V/III ratio. Applying these conditions (772°C, V/III = 6) to growth on a patterned MBE template resulted in near-perfect parallel domain propagation up to 185 microns in a 2-hr run. Growth rates over 150 μm/hr have been achieved at even higher growth temperatures (795°C) while maintaining excellent domain integrity. Successful frequency conversion was achieved for the first time in these crystals: optical parametric oscillators pumped by both 1- and 2-micron lasers produced 4.6-micron idler output.

4:15 PM - 4:30 PM
CONTINUOUS WAVE MID-INFRARED GENERATION BY DIFFERENCE FREQUENCY MIXING IN ORIENTATION-PATTERNED GALLIUM PHOSPHIDE CRYSTAL
Shekhar Guha1, Jacob O. Barnes1, Peter G. Schunemann2
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Difference Frequency Mixing (DFM) is an attractive alternative to Optical Parametric Oscillation (OPO) for generation of infrared radiation by frequency conversion of shorter wavelength lasers. MultiWatt level generation of continuous wave (CW) light having wavelength of 3400 nm by DFM of 1064 nm and 1550 nm lasers has previously been demonstrated in periodically poled Lithium Niobate (PPLN) crystals [1]. Since the values of the d coefficient of cubic semiconductors such as GaAs and GaP are much higher...
than that of lithium niobate, (90 pm/V, 70 pm/V and 25 pm/V, respectively) investigation of quasi-phase matched nonlinear frequency mixing in orientation patterned GaAs and GaP (OPGaAs and OPGaP) is of interest. The calculated values of the required grating spacing for DFG of 1064 nm and 1550 nm in OPGaAs and OPGaP crystals are respectively 8.72 micrometers and 20.7 micrometers [2,3]. For this experiment an OPGaP crystal was available with a grating spacing of 20.8 micrometers, which is very close to the 20.7 micron period predicted for this interaction. The thickness of the grating was about 150 micrometers and the crystal was 5 mm wide and 16.5 mm in length. 1064 nm and 1550 nm CW laser beams were focused by a lens to be simultaneously incident at the center of the crystal. Midwave power in the range of hundreds of microwatts was obtained with tens of watts of incident powers. With better control of beam focusing and sample temperature, higher levels are expected for the generated power. Dependence of the generated power on the polarization directions of the incident beams with respect to the crystal axes will be reported. This is to our knowleded the first report of CW nonlinear optical interaction in OPGaP.

References:

4:30 PM - 4:45 PM
HYDRIDE VAPOR PHASE EPITAXY OF BULK INDIUM GALLIUM ARSENIDE
Peter G. Schunemann, Kevin T. Zawilski
BAE Systems, Nashua, NH

Bulk growth of ternary semiconductors is desirable for applications ranging from custom lattice-matched substrates to infrared optical components. Melt growth of semiconductors from mixed binary melts is plagued by severe segregation that results in compositional nonuniformity, constitutional supercooling, and ultimately interface breakdown and polycrystallinity. Crystal growth from the vapor phase is free from such severe segregation effects, but traditional vapor growth techniques used for III-V semiconductors such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) are characterized by extremely slow growth rates (~1 μm/hour) which are impractical for producing the very thick layers (1000-1500μm) required for producing bulk optical components. Low-pressure hydride vapor phase epitaxy (LP-HVPE) offers all of the advantages of vapor growth (no segregation effects, ultra high purity, superior process control, in-situ diagnostics, low native defect concentrations, etc.) but at growth rates over 100X higher than those typical of MBE or MOCVD: in fact the 100-200 micron/hour rates achieved by HVPE are approaching those used for bulk semiconductor growth from the melt. Here we report the use of LP-HVPE to produce epitaxial InGaAs layers on InAs substrates with compositions ranging from 17 to 32% Ga and thicknesses > 500 microns. Typical growth parameters are as follows: substrate temperature of 600-700°C; reactor pressure of 20 mbar; HCl flow rates of 8 and 32 sccm over Ga and In; AsH₃ flow rate of 120 sccm. Polished layers exhibit near-theoretical optical transmission, band gaps ranging from 0.47 to 0.59 eV, and FWHM rocking curve widths below 3 arcminutes.

4:45 PM - 5:00 PM
CONTROL OF SAPPHIRE CRYSTAL MORPHOLOGY GROWN IN A KYROPOULOS FURNACE
Gourav Sen¹, Thierry Duffar², Guillaume Alombert-Goget², Kheirreddine Lebbou², Nicolas Barthalay², Cyril Pezzani¹, Bruno Delagenière²
¹SIMaP, Grenoble, France,²Institut Lumière Matière, Lyon, France,³RSA le rubis SA, Jarrie/Grenoble, France,⁴Cyberstar, Grenoble, France

The Kyropoulos Method is used to grow large sized titanium-doped sapphire single crystals for power laser applications. However these crystals possess some huge macroscopic defects like bubbles and haze which render a large bulk of the crystal unworthy for use. The crystal shape evolution during the growth process influences the presence of these defects and hence an effort was made to study the crystal shapes as an effect of varying growth parameters. A comparison was made on various grown crystals to establish the relationship between the morphological defects and the growth parameters. An ideal growth process has been defined with the growth parameters for different stages of evolution of the crystal. An automated method of growth process control was developed to maintain those parameters and thus obtain crystals of a superior quality.
GROWTH OF BGaN ALLOYS ON ALN
Michael W. Moseley, Daniel D. Koleske, Stephen R. Lee, Andrew A. Alleman
Sandia National Laboratories, Albuquerque, NM

The introduction of boron into the established group-III nitride materials system provides new degrees of versatility in bandgap, refractive index, and lattice constant engineering. For example, BGaN can theoretically lattice match to AlN and SiC at 8% and 17% boron compositions, respectively. These properties might prove useful in more advanced high-power electronics and short-wavelength optoelectronics. However, there are many challenges in the synthesis of boron-containing nitride alloys, especially achieving large enough boron compositions to lattice match to AlN and SiC. In this study, we report on recent efforts to explore the conditions required for BGaN growth on AlN templates.

The initial growth conditions chosen for BGaN were similar to those already employed for GaN growth: 800 °C growth temperature, 75 Torr growth pressure, a N$_2$/H$_2$ carrier gas mixture, 83 μmol/min of TMGa, and 7 SLM of NH$_3$. The boron composition of the BGaN films mirrored the gas-phase content of the TEB up to 1.83%, as determined by x-ray diffraction, with the diffraction analysis accounting for the biaxial strain state of the BGaN alloy when grown on AlN. A sublinear response in boron composition and a rough surface morphology was observed with the addition of more TEB (>1.75 μmol/min). A boron composition of 3.73% was achieved with a higher NH$_3$ flow of 14 SLM, but a diminishing boron composition and surface roughening were again observed with higher TEB flows (>5.25 μmol/min).

The N$_2$/H$_2$ carrier-gas mixture ratio was then optimized using a constant TEB flow of 7 μmol/min. With the total flow of N$_2$/H$_2$ held constant at 14 SL, the ratio of N$_2$ to H$_2$ was varied and found to have a strong effect on both surface morphology and boron incorporation. In pure H$_2$, the surface was rough and the boron composition was 3.85%. In pure N$_2$, the surface was pitted and the boron composition was 3.75%. However, a growth window of relatively smooth morphology and ~4.2% B was found between 8L H$_2$ / 6L N$_2$ and 5L H$_2$ / 9L N$_2$.

The optimization of the N$_2$/H$_2$ carrier-gas ratio was repeated under other conditions, including 20 SLM of NH$_3$, lower growth temperatures, and higher TEB flows. Through this iterative optimization process, a boron composition of 4.8%, which is very close to the theoretical 5% miscibility gap, was achieved. Ongoing work seeks further improvements in surface morphology and boron composition, with a goal of BGaN lattice match to AlN.
substrates even at high temperatures (1200°C) and with thick deposits (15 µm). XRD showed predominate BP(111) orientations on both types of substrates and other BP orientations were minimal, indicating good crystalline quality. The 28 scan FWHM values of BP(111) decreased with temperature; the lowest value was 0.19° at 1200 °C. SEM showed the increased grain size and improved BP(111) texture with temperature and PH3/B2H6 ratio. Confocal Raman imaging showed the BP films on AlN/sapphire(0001) were more uniform; they exhibited a narrower range of Raman peaks shifted compared to 4H-SiC(0001) and 3C-SiC/Si(100). Rotational twinning in the BP films, due to degenerate epilayer caused by growing 3-fold BP(111) on 6-fold AlN(0001), was confirmed by x-ray topography technique. Preliminary Hall effect measurements of BP on AlN/sapphire(0001) at room temperature showed the films to be n-type with a mobility of 240 cm²/V·s and carrier concentration of 5.0x10¹⁰ cm⁻³. These results suggest that AlN/sapphire(0001) is a good substrate for growing high quality epitaxial BP films.

4:10 PM - 4:30 PM

**EPITAXIAL IcosaHEDRAL BORON PHOSPHIDE GROWN ON VICINAL (0001) 4H-SiC SUBSTRATES**
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The structural variations of the wide bandgap (3.35 eV) semiconductor icosahedral boron phosphide (B₃P₂) grown heteroepitaxially on two types of vicinal 4H-SiC—Si-face (0001) miscut 4° in the [11-20] and [1-100] directions—is reported. While vicinal SiC substrates tilted in the [11-20] direction is the industry standard for SiC homoepitaxy, substrates tilted to the [1-100] may reduce rotational twinning in the growth of 3-fold symmetry materials such as B₃P₂ on 6-fold symmetry 4H-SiC. XRD rocking curves about the (0003) B₃P₂ peak were minimized at 1300 °C with a FWHM value of ~1080 arcsec on both types of substrates. Laue transmission patterns indicated that the preferred epitaxial relationship between B₃P₂ and 4H-SiC is (0001)<11-20>||[1-100]<11-20>. Both pole figures and Laue transmission patterns revealed that at the optimum growth temperature of 1300 °C, one twin orientation predominates in the films. However, films grown on the [1-100] miscut substrates suppressed the formation of the minor twin orientation by a factor of 10 over films grown on substrates tilted in the [11-20] direction. The formation of rotational twins is attributed to the types of SiC step edges made available on each vicinal substrate by a high temperature in situ H₂ etch prior to B₃P₂ epitaxy. Since [1-100] step edges are inherently more stable than [11-20] step edges due to the bonding configuration of SiC, [11-20] steps etch more rapidly than [1-100] steps. In a crystal miscut in the [11-20], the (11-20) steps etch back until two equivalent (1-100) step edges are locally expose, each rotationally offset by 30° in either direction from the [11-20]. By exposing two adjacent (1-100) steps, the hexagonal nature of the substrate is exposed to the film during nucleation, and one of the two rotational B₃P₂ twins can nucleate on each of the (1-100) step edges. By contrast, only one (1-100) step edge can form during etching of the SiC miscut towards [1-100], effectively masking the hexagonal symmetry of the substrate and forcing a single rotational variant of B₃P₂ to nucleate on the only exposed (1-100) step edge. This technique could possibly be extended to heteroepitaxy of other lower symmetry (e.g. cubic (111)) semiconductors on 4H-SiC.

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4:30 PM - 4:50 PM

**NEW ARCHITECTURE TO FABRICATE LARGE PENTACENE SINGLE CRYSTAL FOR HIGH PERFORMANCE ORGANIC FIELD EFFECT TRANSISTORS**
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Because of a better structural ordering for the organic single crystal, the single-crystal OFET have been expected to own the higher carrier mobility than the poly-crystal OFET. Therefore, the single-crystal OFET can be applied to the high-speed organic flexible electronics and also be implemented for clarification of transport mechanisms for organic semiconductor materials. However, the challenges for the high performance single-crystal OFET consist of the achievement of large-sized organic crystal and interface controlling and achievement of better carrier injection from electrodes. In this work, we focus on the achievement of high mobility OFET fabricated using the two-step growth of organic single crystal and an interface controlling. We demonstrated a new strategy to synthesize large pentacene single crystal and to fabricate the single-crystal OFET without any processing of crystal transfer. To optimize the crystalline OFET implementation conditions, a novel growth method was implemented, namely, initial crystallization from small molecular monolayer islands leads to transfer to the nanosized single crystals with an annealing under N2 atmosphere, and subsequent PVT growth on nanocrystals as seeds has implemented to obtain micro-sized crystals with a better interface quality. This optimal device fabrication process guaranteed the high mobility OFET using an organic single crystal. The highest and average mobility was 4.6 cm²/V·s and 2.00 cm²/V·s, respectively. Compared with reported conventional method fabricating pentacene single crystal OFETs on SiO2 dielectric with highest mobility of 2.3 cm²/V·s, it seems that high quality of the semiconductor/dielectric interface, which affects the performance of OSCFETs severely, was kept by our in-situ devices fabrication method. An apparent mobility correlation with the thickness of crystal and orientation was also found. A temperature dependent measurement for single crystal device was also carried out to elucidate the carrier transport properties. The deep understanding of transport mechanism for single crystal OFET may be helpful for further optimizing the design of organic single-crystal transistors for a better device performance.
Layered metal dichalcogenides have received attention as 2D materials beyond graphene. Semiconducting dichalcogenides are particularly attractive since they may enable next-generation low-dimensional electronics benefiting from carrier confinement and other attractive characteristics, such as flexibility and bendability. While transition metal dichalcogenides - particularly MoS2 - have been studied as prototype systems, other materials, especially those incorporating normal metals, have received much less attention.

Here we discuss the structure, electronic properties, and device characteristics of tin disulfide (SnS2), a semiconducting non-transition metal dichalcogenide. We demonstrate the isolation of few-layer and single-layer SnS2. Using aberration-corrected transmission electron microscopy (AC HR-TEM) and other microscopy methods, we establish the characteristics of single- and few-layer SnS2. Band structure measurements in conjunction with photoluminescence and TEM-cathodoluminescence spectroscopy allow us to determine the electronic structure of semiconducting SnS2 and its evolution from the bulk to a single layer [1]. By fabricating field-effect transistors, we explore the achievable carrier mobility and the characteristics of photodetectors, and we identify the factors that govern the performance of SnS2 (opto-) electronic devices.

Electron irradiation in the TEM is used to assess the stability of few-layer SnS2 and study possible electron-beam driven transformations. Electron irradiation has been used to evaluate the radiation response and defect production of 2D materials, and to develop beam-mediated processing techniques. We establish that electron irradiation between 80 and 300 keV invariably affects the structure of few-layer SnS2. Using real-time AC HR-TEM, we follow these structural transformations and show that the associated loss of the chalcogen species (S) accompanies a controlled conversion from Sn(V) to Sn(II) sulfide. Driving this conversion locally with the electron beam creates in-plane 2D heterostructures between different layered sulfides [2].

enhanced technique. We recently described polymer-free process for protecting graphene with a thin precious metal layer during the fabrication. The etchant used to remove the precious metal layer initiates a molecular doping process which reduces the inherent high electron-doping level in EG. The doping level can be restored by annealing in vacuum at moderate temperatures. One of our high-quality, large-scale (5.6 mm x 5.6 mm) octagonal EG devices has demonstrated the possibility of using epitaxial monolayer graphene for the next generation of high-quality quantum Hall effect (QHE) devices. Nowadays, devices used for QHE resistance standards are GaAs heterostructures operated below 1.6 K with current ~50 [µA] in intermediate to high magnetic fields. We observed robust 2 QHE plateaux in the EG device at 9 T magnetic field for temperatures up to 5 K and 3.4 K, respectively, for the two perpendicular orientations of current. Over the magnetic field range 7 T – 9 T, zero longitudinal resistivity was measured at an uncertainty of 150 [µΩ] for temperature 2.7 K and source-drain current 70 [µA]. To our knowledge, this is the first demonstration of a centimeter-scale EG device with high mobility (>3000 cm²/Vs) and near-perfect single-layer uniformity.
MOLECULAR DYNAMICS SIMULATIONS OF PEPTOIDS ADSORBED ONTO CALCITE SURFACES; WHICH MOLECULE-SURFACE INTERACTIONS ALTER CALCITE GROWTH RATES

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Peptoids, or poly N-substituted glycines, are biomimetic compounds for proteins that can be altered by very simple chemistry involving substitutions at the nitrogen and contain less complexity due to their lack of the normally chiral alpha-carbon present in peptides. These molecules are, therefore, very useful as models in experiments studying the effect of the physical and chemical structure of peptides on mineral growth (in the biomineralisation of calcite in aquatic species such as coccolithophores). They are also of interest in promoting the sequestration of carbon dioxide from the atmosphere as calcite. Simulations using several model peptoids discussed in the work by Chen et al [1] have been performed. The experimental work found that peptoids of similar molecular weight had significantly different effects upon the growth and morphology of calcite based on their differences in acidity, connectivity and substitution patterns. Aqueous phase simulations have been completed showing that even in the absence of a surface these molecules act differently, possessing different radii of gyration and diffusion coefficients. We will present calculations involving these peptoids at either stepped, kinked, or flat calcite surfaces to provide an atomistic level insight into the origins of the variation in growth rate and crystal morphology depending on peptoid composition.


OBSERVATIONS OF INTERSTITIAL ATOMS GENERATION NEAR GROWTH INTERFACE DEPENDING ON CRYSTAL PULLING RATES DURING CZ SILICON GROWTH BY DETACHING FROM THE MELT

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In normal CZ crystal growth, since formation of a cone tail takes a long time, it is not possible to assume actual distribution of vacancies (V) and interstitial atoms (I) in a straight body of a crystal during growth. This experiment attempts to observe point defect distribution frozen by rapidly cooling a crystal that has been detached from a melt during growth to eliminate the effect of the time delay.

The 100 mm diameter <100> crystals were grown with the three kinds of pulling rates such as 0.9, 0.75, 0.5 mm/min both for the detached (D) crystals and the normally pulled (F) crystals with tail cones. First, the D type and F type crystals were cut at a position of 70 mm from their shoulder. For specimen wafers cut from the D type crystals, the length from the cut surface to a detached bottom surface was 200 mm. Accordingly, the F type crystals were cut at a position of 270 mm from their shoulder. Then these ingots having a length of 200 mm were sliced into a 1-mm-thickness wafer with a (100) plane. To observe the V and I distributions in the detached crystals, the AOP at 1000°C, 16 hrs. and the IOP + AOP at 800°C, 3 hrs plus 1000°C, 16 hrs annealing have been done, respectively and they were observed by the X-ray topographs. The minority carrier lifetime mapping using µ-PCD exactly coincided with the above I distributions.

Comparison between the defect distributions of the detached crystals and the normally pulled crystals revealed that vacancies are introduced at a growth interface and their concentrations do not depend on the pulling rate. In addition, when the pulling rate is low, Is are generated due to thermal gradient (G) are increased because the amount of heat transfer due to mass transfer is decreased and the surface near the growth interface is cooled for longer period. As a result, the generation of Is due to the increase of the G is observed in an area referred to as an interstitial generation area (IGA) located above the growth interface, where the crystal temperature is 1300°C or more. This paper describes the recombination (Rc) mechanism by which these Is created in the IGA are recombined with Vs transformed through the growth interface, thereby creating an observable recombination area at a location where their concentrations are identical.
THE ROLE OF CRYSTALLITE WITHDRAWAL RATE AND EXTERNAL HEAT AND MASS SOURCES DURING SOLIDIFICATION IN NUCLEATION AND CRYSTAL GROWTH PROCESSES
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Objectives. Industrial production of many kinds of materials from super-cooled melts and supersaturated solutions is very important for many metallurgical, chemical and pharmaceutical products. The final goal of every industrial crystallization process is to obtain crystals of a given size, shape, composition, and internal structure. This goal is achieved using a variety of methods based on the main mechanisms: nucleation of crystals and their subsequent growth. Our objective is to provide a deeper understanding of these processes, which would be of great importance in relation to the nucleation and crystal growth phenomena as well as to the design, operation and control of industrial crystallizers.

Method. A non-linear time-dependent integral equation with memory kernel for the metastability level is analytically solved on the basis of the saddle-point method for the Laplace integral in the case of mixed kinetic-diffusion regime of crystal growth, which is of frequent occurrence.

Results. A complete analytical solution of the integro-differential model describing the transient nucleation and growth of the crystals at the intermediate stage of phase transitions is constructed. The roles of external heat/mass sources appearing in the balance equations and the crystallite withdrawal rate entering in the Fokker-Planck equation are detailed. An approximate analytical solution of the Fokker-Planck equation is found with for allowance the diffusion of the distribution function in the space of crystal radii for arbitrary nucleation mechanisms and growth kinetics. Two important cases of the Weber-Volmer- Frenkel-Zel'dovich and Meir kinetics are considered in some detail. It is shown that the desupercooling/desupersaturation rate decreases with increasing the crystallite withdrawal rate and intensities of external sources.

Conclusion. The density distribution function becomes more and more broad with time. In addition, this function increases with decreasing the crystallite withdrawal rate and with increasing intensities of external sources.

Outcome. The formation and evolution of nuclei in batch crystallizers is essentially a dynamic process controlled by the competition among the crystal withdrawal rate, the intensity of external heat (mass) sources and the rate of metastability reduction, which is dependent on both the nucleation frequency and growth rate of crystals.
Metal-organic crystal bis(hydrogenmaleate)-Co(II) tetrahydrate single crystals have been grown by slow evaporation solution growth technique at room temperature. The crystal structure and the unit cell parameters were analyzed from the X-ray diffraction studies. Single-crystal X-ray diffraction analyses reveal that the grown crystal belongs to triclinic system with the space group P1. Functional groups in bis(hydrogenmaleate)-Co(II) tetrahydrate were identified by Fourier transform infrared spectral analysis. The peak observed at 663 cm⁻¹ is assigned to the (Co-O) stretching vibrations. The optical transmission of the crystal was studied by UV-Vis-NIR spectral analysis. The photoluminescence emission studies were carried out for the title compound in a wide wavelength range between 350 nm and 550 nm at 303 K. Mechanical strength was tested by Vickers microhardness test. The Laser damage threshold value has been determined using Nd:YAG laser operating at 1064 nm. The dielectric behavior was investigated at various frequencies and temperatures. Solid state parameters such as plasma energy, Penn gap, Fermi energy and electronic polarizability were evaluated. Photoconductivity measurements were carried out for the grown crystal in the presence of DC electric field at room temperature.

5:00 PM - 7:00 PM
BULK GROWTH AND CHARACTERIZATION STUDIES OF NOVEL SEMI ORGANIC PIPERAZINUM HYDROGEN SUCCINATE SINGLE CRYSTAL
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The new semiorganic third order nonlinear optical material piperazinium hydrogen succinate (PPHS) was synthesized by slow evaporation method. The material solubility was determined by gravimetrical analysis and metastable zonewidth was assessed by polythermal method. The nucleation and its related parameters gave an idea about the crystal growth process, and optimized condition for the growth of large size single crystals. Induction period was measured by following isothermal method. The nucleation parameters such as interfacial energy, Gibbs free energy, number of critical nuclei, number of molecules present in the critical nucleus and also nucleation rate were determined for the grown crystal [1]. As an outcome of studying nucleation parameter, bulk single crystal of PPHS was grown by slow cooling method. The single crystal XRD analysis confirms the crystalline nature of PPHS and its lattice parameters were estimated [2]. The structure of PPHS was refined by using ShelX. The various vibrational modes of different functional groups were identified and their wavenumbers were assigned from FT-IR and FT-Raman spectrum analyses. The number of proton and carbon were present in the title compound was assessed by FT NMR analysis. The cut off wavelength of the PPHS crystal was found to be 254 nm from UV-Vis-NIR spectrum. Tauc's plot energy bandgap was determined as 4.86 eV. Also the various optical parameters were calculated by using standard relations [3]. Photoluminescence behavior of PPHS was studied. The thermal stability of the compound was determined by TGA analysis. The dielectric behaviors of the crystal by varying frequencies at different temperatures were studied. The mechanical strength of the grown crystal was found from vickers microhardness tester. The meyer’s index number was determined from hardness value. The hardness related parameters were also calculated. The third order nonlinear optical property of PPHS crystal was estimated by using z-scan technique.

References

Supplementary data
Full Crystallographic data (cif file) relating to the crystal structure have been deposited with the Cambridge Crystallographic Centre as CCDC No. 1007637. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; E-mail address: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
SYNTHESIS BULK GROWTH AND CHARACTERIZATION ON COMPLEX METAL ORGANIC SODIUM BORO OXALATE SINGLE CRYSTAL A THIRD ORDER NONLINEAR OPTICAL MATERIAL

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Several stable complexes of boron is frequently increased by the addition of polyhydroxy compound, which give rise to the formation of complex compound. The acid-base equilibrium and electrolytic conductivity have confirmed by the presence of negative complex ions containing boron. As a continuation in the process of systematic approach of research into the boron complexes with polyhydroxy compound to prepare well-shaped single crystals, Sodium boro-oxalate (NaBC4O8) was synthesized by slow evaporation method. The crystalline nature and the structure of the grown crystal was determined by powder X-ray diffraction (PXRD) and single crystal X-ray diffraction (SXRD) technique. The existence of the functional groups present in the grown crystal was confirmed by Fourier transform infrared (FT-IR). The UV-Visible-NIR spectrum explains about the transmission properties of the material. Optical band gap was calculated by using Tauc’s plot. The thermal stability of the grown crystal was studied by using thermogravimetric analysis (TGA) and the eutectic point, melting point and decomposition point were revealed by differential scanning calorimeter (DSC). The dielectric constant and dielectric loss were studied as a function of various frequencies at different temperature. The grown crystal was subjected to Vickers microhardness test to estimate the hardness properties. The hardness related parameters such as Elastic stiffness constant (C11), Fracture toughness (Kc), Brittleness index (Bi) and Yield strength (σy) were calculated. The third order nonlinear optical properties of the grown crystal was determined by Z scan technique.

References

GROWTH OF CA3NBGA3SI2O14 PIEZOELECTRIC CRYSTALS GROWN FROM CONGRUENT COMPOSITION

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Ca3NbGa3Si2O14 [CNGS] single crystal have been investigated as a piezoelectric material for combustion sensor and small-size oscillator with low electrical consumption. The CNGS piezoelectric crystal indicated higher piezoelectric constant than quartz from room temperature to 1000 °C. In addition, the crystal impedance of the CNGS element is smaller than that of quartz and the temperature coefficient of frequency (TCF) is comparable to the quartz. We have developed shape-controlled CNGS piezoelectric
crystals by the micro-pulling-down method to reduce the cost of manufacturing. However, the grown CNGS crystal included secondary phase in the periphery area. The result suggests the stoichiometric composition of CNGS is not consistent with the congruent composition, and the difference between stoichiometric and congruent compositions generated the secondary phase. Therefore, in this study, we investigated the congruent composition of CNGS and the CNGS crystal was grown by the congruent composition.

CNGS crystals were grown by the μ-PD method using powders with stoichiometric and congruent compositions. Mixed powders were prepared from starting materials, CaCO3, Nb2O5, Ga2O3, SiO2 and α-Al2O3 powders (> 4N purity) as stoichiometric and congruent compositions. Congruent composition was determined by the analysis of chemical composition of CNGS crystal grown by Czochralski method. The mixed powders were sintered at 1200°C for 12 hours in air several times. Fiber crystals were grown using Pt-Rh crucible and CNGS seed crystal in Air. Grow crystals were cut and polished for measurements of local structure, chemical composition and piezoelectric properties. Phases and lattice parameters of grown crystals were identified by powder X-ray diffraction measurement. Chemical compositions were analyzed by the electron probe micro-analysis and inductively coupled plasma analysis.

CNGS crystals were grown from the starting material with congruent composition by the μ-PD method and the as-grown crystal indicated high transparency. In addition, the grown CNGS crystal didn’t include visible inclusion in the crystal. The result revealed that the congruent composition was not consistent with the stoichiometric composition and the crystal without inclusion could be obtained from the starting material with the congruent composition. The detail of crystal growth and the properties of grown CNGS crystals will be reported.

5:00 PM - 7:00 PM
PHASE TRANSITION AND DIELECTRIC PROPERTIES IN HIGH-STRAIN ZR-DOPED 92.5%(Bi0.5Na0.5)TiO3-7.5%BaTiO3 PIEZOELECTRIC SINGLE CRYSTALS
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Lead-free piezoelectric materials such as Bi0.5Na0.5TiO3-BaTiO3 (BNBT) solid solution have been attracted many attentions due to the environmental perspective. The morphotropic phase boundary (MPB) around 6~7 mol% BT, separating rhombohedral (R) and tetragonal (T) phases, exists in the (1-x)(Bi0.5Na0.5)TiO3-x(BaTiO3) system accompanied by a significant enhancement in the dielectric and piezoelectric properties, which are more than or close to the performances of PZT ceramics [1]. The piezoelectric performances of BNT variants are expected to be further enhanced by doping zirconia [2]. The perovskite (Bi0.5Na0.5)0.925Ba0.075Ti1-yO3 (BNB100yT) single crystals have been grown for y=0, 0.02 and 0.04. To maintain the high purity of the crystal, a self-flux method was employed with one of the elements of the compound as a flux. The crystals were grown in a platinum crucible at 1300 °C. Cooling rate was 1 oC/h. The as-grown crystals are cubic in shape or orthorhombic forms, and are lightly yellow in color but transparent. Compared with BNBZ0T (y=0) crystals, self-flux growth of the zirconia containing compositions resulted larger crystals. Lower Zr doping levels (y=0.02) have yielded higher quality crystals. In this work, characterizations of dielectric permittivity, ferroelectric/piezoelectric properties, phase transition, and polar nanoclusters are measured for BNBZ100yT crystals. Based on results of X-ray diffraction and dielectric measurements, structural coexistence of rhombohedral (R) and tetragonal (T) phases (y=0) and pseudo-cubic phase (y=0.02) crystals have been obtained and do not show significant polarization or field-induced strain hysteresis characteristics. A frequency-dispersive dielectric response characteristic of a relaxor ferroelectric is observed as a function of temperature. The dielectric permittivity (ε') of (001)-oriented (Bi0.5Na0.5)0.925Ba0.075Ti1-yO3 (BNB200yT) crystal is ε'~1500, which is larger than ε'~620 in (001)-oriented BNT single crystal for measuring frequency f=1 MHz at room-temperature [3]. The temperature dependent dielectric properties of BNBZ0T and BNBZ4T crystals showed relaxor-like behaviors. The remnant polarization, coercive field, and piezoelectric properties were found to decrease by the substitutions of 2 and 4 mol % Zr4+ for Ti4+ in these crystals.

References

5:00 PM - 7:00 PM
PECULIARITIES OF GROWING BULK BAY2F8 AND SrAlF5 SINGLE CRYSTALS FOR APPLICATION IN UV AND VUV SPECTRAL REGIONS
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Inorganic single crystal fluorides are the most promising materials for applications in the UV and VUV parts of the spectrum, as they have the most short-wave limit of own transparency in comparison, for example, with oxide compounds. Also, the fluoride single crystals are characterized highest chemical stability compared with other classes of compounds. These properties define the broad scope of alkaline earth fluorides and LiF in the optical industry as materials of geometrical optics for shortwave spectrum. However, the use of fluoride crystals in technique now limited by the lack of reliable growth technologies of fluoride single crystals of the specified quality. The aim of this work is to develop a techniques for growing single crystals BaY2F8 and SrAlF5 specified quality and sizes. The report will cover the following topics
1. General principles for growing single crystals of inorganic fluorides. Will be discussed in comparison the methods of growing crystal fluorides from the melt: Bridgman, zone melting and Czochralski, and will show that for growth of fluorides best of them is the method of Bridgman. The problems of selection of construction materials, different designs of the heating blocks to create figured temperature gradients, the optimal environment to grow the
fluorides.

2. Effect of preparative aspects on the transparency in the VUV region of the spectrum.

Will show a link between limit of transparency of crystals, content of basic impurities and oxygen concentration (the most influential impurity) in the crystal lattice. Determined allowable concentration of oxygen impurity in the matrix crystals BaY2F8 and SrAlF5 for their work in the UV and VUV spectral ranges.

3. Features of the activated crystals BaR2F8 growth to excite UV and visible luminescence by infrared laser diodes.

Will covered the issues of overheating and overcooling melts, the doping by rare-earth ions with isomorphic and no isomorphic inclusion their in the crystal lattice. The technique of growing oriented crystals BaR2F8 and the luminescence in the visible and UV region excited by IR laser diodes will presented.

4. Features of the crystals SrAlF5 growth.

Will focused on decomposition of melts SrAlF5 and ways to overcome this problem. The technique of crystal growth and the spectra of intrinsic transparency in the VUV region will presented.

5:00 PM - 7:00 PM
CZOCHRALSKI GROWTH OF 2 INCH CA3Ta[GA,Al]3SI2O14 SINGLE CRYSTALS FOR PIEZOELECTRIC APPLICATION
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The crystals of langasite-type structure family are currently considered as well-known piezoelectric materials. They have no phase transitions up to their melting points (over 1000°C). Therefore, they are suitable for high-temperature applications including temperature sensors and combustion engines. Many langasite type crystals melt congruently. According ly, they can be grown by conventional Czochralski technique that makes these materials industrially friendly. Moreover, they demonstrate high piezoelectric constants exceeding those of the quartz two-three times. Furthermore, it is reported that the ordered langasite-type structure, such as Ca₃Ta₃Ga₃O₁₄, Sr₃Ta₃Ga₃O₁₄, Ca₃NbGa₃Si₃O₁₄ and Sr₃NbGa₃Si₃O₁₄, shows higher homogeneity of acoustic velocity.

Ca₃Ta[GA,Al]₃SI₂O₁₄ single crystal (CTGAS) belongs to langasite family and ordered structure crystals possesses a number of unique piezoelectric characteristics that enable its application in the development and manufacture of piezoelectric devices such as oscillators, BAW resonators and so on.

In this study, growth of 2-inch diameter Al-substituted Ca₃Ta₃Ga₃O₁₄ crystals by Czochralski method is reported. The melts used contained equal amounts of beta-Ga₂O₃ and alpha-Al₂O₃ corresponding to chemical formula of Ca₃Ta₃Al₂Si₃O₁₄. The Ca₃Ta[GA,Al]₃SI₂O₁₄ crystals produced using non-substituted Ca₃Ta₃Ga₃O₁₄ seeds were highly defected with cracks or had polycrystalline phase. However, those grown on the seed of approximately Ca₃Ta₃Al₂Si₃O₁₄ composition were defect-free. The growth proceeded from iridium crucible of 100 mm in outer diameter that was heated inductively using radio-frequency (RF) coil powered from a generator. It is noted that increase of Al content in the CTGAS compound increases its melting point as it was generally expected. Phase diagram of the Ca₃Ta₃Ga₃O₁₄ - Ca₃Ta₃Al₂Si₃O₁₄ pseudo-binary system is discussed in some details. Homogeneties of the grown CTGAS crystal is characterized using the line-focus-beam ultrasonic-material-characterization (LFB-UMC) system.

5:00 PM - 7:00 PM
ANALYSIS OF THE ACCELERATED CRUCIBLE ROTATION TECHNIQUE DURING THE BRIDGMAN GROWTH OF CADMIUM ZINC TELLURIDE
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The application of the Accelerated Crucible Rotation Technique (ACRT) is an essential strategy for the growth of mercury cadmium telluride. However, there are far fewer cases of its use during the Bridgman growth of cadmium zinc telluride (CZT), perhaps due to challenging technical issues for the larger growth systems necessary to produce crystals suitable for gamma radiation detectors. Nevertheless, there is strong motivation for ACRT growth of CZT, particularly to reduce the formation of large, second-phase, tellurium-rich particles. These particles are deleterious to the performance of detectors, and current practice applies long, post-processing anneals to reduce their size in CZT crystals. The high efficiency of melt mixing driven by ACRT acts to stabilize morphological instabilities of the growth interface, thus reducing the potential for inclusion processes that may lead to the formation of these unwanted particles. Such an approach promises for faster growth with higher yield, thus reducing the cost and increasing quality of detector material.

This poster will report initial results on a collaborative research project between the University of Minnesota (UMN) and Washington State University (WSU). Preliminary growths at WSU have indicated nearly uniform radial zinc distribution and a shift in the mean inclusion size, both of which can be attributed to more uniform melt mixing upon accelerated crucible rotation. Further optimization of the rotation scheme based on feedback from computational work at UMN is expected to improve axial solute/dopant segregation and further reduce the second phase defect size. Computation will explore the ability of ACRT to reduce the prevalence of tellurium-rich second-phase particles in grown material as well as the ability to achieve and maintain a convex interface shape during growth.

Our model employs the CrysMAS software package (Fraunhofer IISB) coupled with our finite element code Cats2D to predict furnace heat transfer and conditions for crystal growth within the ampoule. Of particular interest are the complex, time-dependent flows that arise from the application of accelerated crucible rotation. Toward designing an optimal rotation schedule for CZT growth in this system, we consider strategies to dynamically adapt the rotation schedule to the different temperature gradients and melt arc conditions, which determine the form and strength of the underlying buoyant flow, that arise during the lifetime of a growth run. This work is supported by the Department of Energy, National Nuclear Security Administration, under Award DE-NA0002565; no official endorsement should be inferred.
5:00 PM - 7:00 PM

**NON-POLAR (10-10) AND SEMI-POLAR (10-11) GaN TRULY BULK GROWN BY HVPE**

Aleksey Pechnikov, Vladimir Nikolaev

“Perfect Crystals” LLC, Saint Petersburg, Russian Federation

Non-polar (10-10) and semi-polar (10-11) GaN truly bulk grown by HVPE

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HVPE nonpolar and semipolar GaN quasi-bulk substrates are presently very small in size and expensive because they are sliced vertically from a thick c-plane GaN substrate. Probably due to progress in nonpolar and semipolar ammonothermal GaN bulk it is no competitor for future LED substrates.

In this work we demonstrate new HVPE GaN truly bulk on seeds. The seeds were GaN layers grown on m- and R-sapphire, which self separated from sapphire after cool-down. GaN bulk crystals were grown using special HVPE multistep growth. The resulting GaN crystals were studied. X-ray analysis revealed that actually two orientations (semi-polar and non-polar) can be dominated. It depends on the seeds and controlled by modification of initial sapphire surface in chemistry and/or growth procedure. There is a difference in morphology of semi-polar and non-polar bulk crystals. The quality of all crystals grown in both cases is able to improve by following re-growth.

Figure 1 The optical image of (10-10) GaN bulk

Figure 2 SEM image of the GaN bulk
Chemical Composition Characterization of Ca$_3$Ta(Ga$_{0.5}$Al$_{0.5}$)$_3$Si$_2$O$_{14}$ Single Crystal by the Line-Focus-Beam Ultrasonic Material Characterization System

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Langasite-type (La$_3$Ga$_5$SiO$_{14}$; LGS) crystals are attractive piezoelectric materials as combustion pressure sensors operating at high temperature environment as well as high stability oscillators and filters using acoustic wave devices. So far, however, they still have not reached the commercial success because the crystals are difficult to grow homogeneously due to their complex chemical composition. It is important to establish a method for evaluating crystal homogeneity and growing homogeneous crystal to realize actual devices mentioned above.

We have developed an ultrasonic microspectroscopy (UMS) technology using a line-focus-beam/plane-wave ultrasonic-material-characterization (LFB/PW-UMC) system. We demonstrated that this technology is capable of evaluating the homogeneity of piezoelectric trigonal single crystals such as LiNbO$_3$, LiTaO$_3$, and α-quartz through measurements of their acoustic properties and of accurately determining their acoustical physical constants. In this study, we extended our technology to homogeneity evaluation of langasite-type crystals taking Ca$_3$Ta(Ga$_{0.5}$Al$_{0.5}$)$_3$Si$_2$O$_{14}$ (CTGAS).

We prepared CTGAS single crystal ingot grown along crystallographic Y-axis direction by Cz method. The crystal size is 1 inch $\times$ 60 mm$^2$. X-, Y-, and Z-cut plate specimen was prepared from the crystal ingot. For these specimens, we measured velocity of leaky surface acoustic wave (LSAW) propagating on a water loaded specimen surface at 225 MHz using the LFB-UMC system. We also measured chemical composition distributions along diameter and pulling axis directions for these specimens by the electron probe microanalyzer (EPMA). We observed LSAW velocity variations in a concentric pattern (those of peripheral part of the ingot were higher than those of central part by 7.8 m/s for Y-cut Z-propagating LSAW at maximum). From the results of the EPMA, the velocity variation deeply related to that in Al-content. The resolution of LSAW velocity to Al-content is ±0.005 mol%, it is higher than that of...
the EPMA (±0.1 mol%). For the result of Y-cut X-prop. LSAW, we observed velocity increase at the peripheral part of the ingot due to decrease in oxygen-content. We hope our ultrasonic technology will make a great contribution to the field of crystal growth.

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NUMERICAL INVESTIGATION OF THE AXIAL OXYGEN CONCENTRATION DISTRIBUTION IN SILICON CRYSTAL DURING CZOCHRALSki GROWTH WITH A TRANSVERSE MAGNETIC FIELD
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A three-dimensional simulation model is used to study the oxygen concentration distribution in silicon crystal during the Czochralski growth process under a transverse uniform magnetic field. The flow, temperature, and oxygen concentration distributions inside the furnace are calculated for different crystal lengths. There is significant variation in the flow structure in the melt with the growth length. The results show that in the initial stages, there is a decrease in the oxygen concentration at the melt-crystal interface as the length of the growing crystal increases. With a further increase in the growth length of the crystal, a minimum value is reached and then the oxygen concentration increases continuously. This trend is consistent with the experimental one. The variation of the oxygen concentration with the growth length is strongly related to the depth of the melt in the crucible and the flow structure inside the melt. Better uniformity of the axial oxygen concentration can be achieved by proper adjustment of the crucible rotation rate during the growth process.

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HYDROTHERMAL GROWTH OF FINE MAGNETITE AND FERRITE CRYSTALS
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Hydrothermal growth of magnetite and ferrites is quite old and in recent years, the subject is becoming more attractive owing to its popularity in technological applications. The growth of magnetite especially is more challenging because of the reduced conditions required in the growth of phase pure magnetite without the formation of hematite. Both magnetite and ferrite could be grown under mild temperature and pressure conditions in the temperature range 150 to 200oC and pressure either autogeneous or <30 atms. The conditions required for the controlled growth of magnetite and ferrite single crystals have been evaluated in the presence and absence of various surface modifiers and biological molecules. The products obtained have been characterized systematically using powder XRD, FTIR, TGA/DSC, photocatalytic properties with respect to the degradation of various organic dyes and also study of various biological assays. The results have been discussed with respect to the process parameters.

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SIZE AND SYNTHESIS EFFECTS ON THE CRYSTALLINE STRUCTURE OF BARIUM TITANATE
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Ferroelectric nanoparticles, in particular barium titanate (BTO), exhibit bewildering behavior at the nanoscale. In sintered, fully dense devices, their permittivity drops off with decreasing grain size from a maximum at μm and larger grain diameters. However, when BTO particles remain unsintered and are studied in solution or some other matrix material, their permittivity has been shown (although these results remain controversial) to increase dramatically as a critical diameter is approached, after which the particles’ permittivity falls precipitously with further decreases in size. Even below this critical size where measured permittivity values of BTO nanoparticles are extremely low and approach zero, some BTO samples have been shown to have tetragonal crystallographic distortions at the local level. However, these tetragonal distortions are not maintained coherently across the entire width of the particle, resulting in a macroscopic crystal structure that resembles a distorted cubic lattice. To date, little is known about how synthesis methods, passivating ligands, and other physical properties of BTO nanoparticles affect their behavior at the nanoscale. We will present a study of several different sets of BTO nanoparticles including commercially available particles produced using hydrothermal routes and solution synthesized BTO produced in our laboratories. The particles cover a range of diameters from 10 to 500 nm and were studied using synchrotron based XRD analyzed using the PDF method, XAFS, and Raman spectroscopy. The results from high energy X-ray and Raman experiments will be compared to other measured physical properties of these particles. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

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INVESTIGATION OF IONIC CONDUCTIVITY OF LANTHANUM CERIUM OXIDE NANO CRYSTALLINE POWDER SYNTHESIZED BY CO PRECIPITATION METHOD
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Lanthanum (La) doped Ceria (CeO\textsubscript{2}) electrolyte has attracted considerable interest, as a candidate material for solid oxide fuel cells (SOFCs). The ionic conductivity of La doped CeO\textsubscript{2} system (La\textsubscript{x}Ce\textsubscript{1-x}O\textsubscript{2}) nano-particles synthesized by co-precipitation method has been investigated. The cubic fluoride structure was observed from the structural analysis of the material. Morphology of the calcined powder and microstructure of the sintered pellets are observed by and scanning electron microscope (SEM), respectively. From the results of impedance spectroscopy from temperature range of room temperature to 400º C, the oxide ion conductivity and density of
proton charge carrier was measured. Thermogravimetric analysis (TGA) was performed on the material to check stability of phase at high temperature. The TG-DSC analysis of the material revealed both oxide ions and protons contribute to the total conductivity.

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THE OPTICAL PROPERTY OF NANO-SIZED INGAN/GaN POLARIZED LIGHT EMITTING DIODES
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The optical property of nano-sized InGaN/GaN polarized light emitting diodes
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It is crucial to fabricate nano photonic devices such as nano-LED in order to meet the requirements for the integration of photonic and electronic circuits on the nanometer scale [1-3]. The great difficulty is to fabricate traditional LED down to nano-size. Moreover, polarized light has numerous practical applications, especially in imaging industry. Therefore, nano-sized polarized LEDs have gained growing population in the past decade due to their unique and tunable nature for nanophotonic and nanoelectronic applications. Here, we demonstrate an easy method to fabricate single nanorod polarized LEDs based on traditional InGaN/GaN epi-wafer grown on c-sapphire. In order to form nanorod structure, nano-imprint lithography technique and standard inductively coupled plasma (ICP) etching were applied on conventional InGaN/GaN MQWs grown on patterned c-sapphire substrates by metal-organic chemical vapor-phase deposition (MOCVD). After that, nanorods were mechanically removed from the substrate into alcohol solution by ultrasonication. A few drops of the solution were put on prefabricated metal pad on silicon wafer. And finally, the n and p contacts were made by focused ion beam (FIB). The sample structure is illustrated by Fig. 1. The luminescence property of single nanorod LED is shown as Fig. 2. It is found that the nanorod LED can directly generate strong polarized light in contrast to the conventional planar LED as shown in Fig. 3. This method provides an easy way to fabricate nano-sized polarized LEDs based on traditional InGaN/GaN epi-wafer growth instead of the difficult nanorod growth. The n and p type GaN doping will be much better than that in grown nanorod, resulting in lower operating current, which indicates less leakage and better crystal quality.

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STUDY OF PHOTOCATALYTIC AND MAGNETIC PROPERTY OF CO, MN METAL IONS DOPED NANOCRYSTALLINE TIO2 PREPARED BY SOL-GEL METHOD.
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we report the growth of [Mn, Co]xTiO2 (x=0.01, 0.02 & 0.04) nanocrystals prepared by Sol-Gel technique, followed by freeze-drying treatment at -30°C temperature for 12hrs. The obtained Gel was thermally treated at different temperature like 200,400,600, 800°C. The crystalline size of 4 to 40 nm is achieved. X-ray diffraction pattern of samples show anatase phases of TiO2, up to 600°C. At 800°C, the phase is Rutile. The diffraction peak at 25.22°, 25.49°and 25.6° observed from the XRD pattern of the Mn, Co doped TiO2 shows that the main crystal phase is anatase, and the peak at 27.47° indicates the presence of the rutile phase. All the peaks in the XRD patterns of the sample calcined at 200°C, 400°C and 600°C of TM doped TiO2 can be designated to the anatase phase (most active phase) without any indication of other crystalline phases such as rutile or brookite. As a variant valence metal cation, Mn, Co ions can react with Ti4+ on the surface of TiO2, and Ti4+ is reduced to Ti3+ which inhibits the transformation of anatase to rutile. It leads to the reduction in the oxygen vacancies on the TiO2 surface and suppresses the crystallization of other phases by adsorbing onto the surface of the TiO2 particles. The photocatalytic degradation of formaldehyde has been successfully demonstrated using a 250 V UV lamp with TM doped TiO2 nano powder in a specific experimental setup. The degradation rate increases linearly with dopant content. This indicates that the photocatalytic reaction in this experiment was effected by dopant concentration. The results obtained in this research contribute to the understanding of binary doped transition metal ions in TiO2 nanoparticles which can lead the efforts of enhancing their environmental application. Study of magnetic property has been carried out by using VSM. The magnetic susceptibility of the Mn, Co doped TiO2 nanopowder increases with increase in doping concentration. Mn, Co doped TiO2 exhibits ferromagnetism at room temperature.

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PECVD GROWTH AND CHARACTERIZATION OF SI NANOWIRES
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Low-dimensional nanostructures, such as nanowires (NWs) have received significant interest in recent years for a number of applications ranging from energy conversion, to energy storage, to sensors and to emitters among other applications. We have investigated the low pressure plasma enhanced chemical vapor deposition (PECVD) growth of Si nanowires deposited on various substrates at the temperature in the range from ~400 to 600°C. A vertical downward flow reactor was used with the wafer mounted on a pedestal perpendicular to the flow. Growth of Si nanowires included evaporated and colloidal Au seeding as well as self-seeding of nanowire growth. Substrates included Si, ZnO, stainless steel, and TiN coated Cu foils, among other substrates. Si films were grown unintentionally doped, as well as n- and p-type doped. Structures grown include linear nanowires, bifurcated nanowires, and curved nanowire structures. Growth nanowire arrays are characterized structurally and electrically and are related to process parameters.

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BN FILM GROWTH USING PLASMA ENHANCED AND THERMAL CVD PROCESSES
2-D materials have recently received increasing attention for their potential use in electronic devices. In particular, heterojunctions of h-BN and graphene could significantly improve graphene FET and tunneling device transistors. We have explored large area thermal CVD growth of h-BN at reduce pressure at temperatures up to 1350°C in a high speed rotating disc reactor and inductively coupled plasma enhanced CVD at ~600°C. Growth, in both cases, used gas source precursors of diborane - B2H6 and ammonia - NH3. Depositions were primarily carried out on sapphire (0001) substrates. Thermal CVD was also explored using ammonia borane precursors on copper substrates. All processes yielded h-BN, of different quality, as determined by Raman spectroscopy. We herein review the growth processes and resulting films.

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EFFECT OF WIDE BAND GAP TUNNEL DIODES ON THE CHARACTERISTICS OF INGaP/InGaAs/Ge TRIPLE JUNCTION SOLAR CELLS
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As an effort to improve the conversion efficiency of InGaP/InGaAs/Ge triple junction solar cells, we investigated the effect of wide band gap tunnel diodes such as AlGaAs and InGaP layers on the cell performance under concentrated light condition. Two different solar cells have upper junctions (TJs) as n⁺-GaAs/p⁺-AlGaAs layers (sample A) and n⁻-InGaP/p⁺-GaAs layers (sample B) were prepared. In these samples, p⁻-AlGaAs barrier layer was used, which was found to be effective to improve the cell performance. We first optimized the growth conditions of InGaP layer. Then, measurements were performed for the fabricated solar cells. Under concentrated light condition, open-circuit voltage (Voc), fill factor (FF) and conversion efficiencies were measured. Further information on the quality of the solar cells was provided by external quantum efficiency (EQE) measurements. Compared to sample A (8~10%), the conversion efficiency of sample B (>20%) showed the higher value. Based on these results, further investigation will be discussed later.

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EFFECT OF SURFACE RECONSTRUCTION ON GE-Si(001) HETEROEPITAXY
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The most widely studied heteroepitaxial system is Ge on Si(100), due to its ease for integration with Si-based devices. The (100) surface of Silicon shows several reconstructions, of which the 2 × 1 is the most relevant for growth at high temperature in Molecular Beam Epitaxy (MBE). Surface reconstruction changes the nature of bonding on the surface inducing additional anisotropies in surface energy and affects properties of the growing film.

We have developed a two component three dimensional solid-on-solid model on simple cubic lattice, with necessary modifications to account for surface reconstructions. Additionally, the elastic effects due to lattice mismatch between the film and the substrate are modeled using a harmonic ball and spring model of elasticity. This model allows to explain most of the features of Si on Si(001) homoepitaxy like dimer chain formation, island size and shape distribution and their dependence on temperature[1]. In the case of Ge on Si(001), this model is able to reproduce strain induced effects like dimer chain vacancy formation and alignment of vacancies around 1ML coverage[2]. In this study we have revealed how elastic effects, coupled with reconstruction can explain the observed behavior at the early stages of growth of Ge on Si(001).

We have extended the simulations to multilayer growth to study how reconstruction plays a role in the 2D/3D growth transition. Our goal here is to see if it can be used to accurately predict formation and shapes of quantum dots which are formed during Stranski-Krastanov growth.

References

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EXPERIMENTAL STUDY OF GROWTH MECHANISM OF GAAS MICROCHANNEL EPITAXY
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Microchannel epitaxy (MCE) is one of the excellent ways for reducing dislocations in hetero epitaxy [1]. In MCE, a narrow channel, called as “microchannel”, is cut in a mask for selectively and laterally growing an epitaxial layer. A dislocation-free area is obtained on the laterally grown area because the mask terminates the dislocations. Dislocation-free areas of GaAs, InP and GaN have been successfully obtained using MCE. A high lateral to vertical ratio of the grown layer is important to obtain a wide dislocation-free area. In order to increase the ratio, a lot of studies have been performed. However, the growth mechanism has not been quantitatively clarified yet. The atomically flat top surface of the MCE layer is quite suitable for observing the surface spiral steps. Therefore, in this study, the shape of the spiral steps is used to experimentally estimate the surface supersaturation of GaAs MCE. The mechanism is quantitatively discussed using the relation between the vertical growth rate and the surface supersaturation.

The vertical growth rate was found to have a strong relation to the surface supersaturation, where the vertical growth is almost stopped below the critical value. On the other hand, the vertical growth rate linearly increases with the supersaturation above the value. The mechanism is ascribed the pinning effects of the dopants on the movements of the surface steps. In other words, the movement of the surface steps was suppressed, and the vertical growth was stopped. With the surface supersaturation larger than
the critical value, the steps begin to pass through the pinning sites when the critical nucleus radius is smaller than the half of the separation of the pinning sites. Another experimental result shows the pinning effect will disappear on non-doped samples. Finally, a very high aspect ratio of more than 60 was accomplished by the optimization of the growth parameters, according to the deduced growth mechanism.

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FORMATION OF Cu2ZnSnS4 FILMS ON SILICON
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Formation of Cu2ZnSnS4 films on silicon.
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This paper reports the study of formation of thin CZTS films on Si. Formation of CZTS films was carried out in two stages. During the first stage, the precursors were formed, using a vacuum deposition method, on a single crystal silicon wafer with crystallographic orientation of (111) or (100). At the second stage, the precursor was sulfurized from an unlimited source in a closed container. The components were deposited on silicon either sequentially or concurrently, with varying sequence of components under sequential spraying deposition. Thermal annealing was carried out at temperatures from 400 to 620°C, duration of annealing was in the range of 15-60 minutes. The heating rate was 15–30 deg/min.

It was found that smoother surface is obtained with the deposition of the components in tin-zinc-copper sequence and annealing temperatures of 530–550°C. In other cases, there is some roughness on film surface that appears to be due to the volatilization of certain components of the (S, Zn)-compound.

In the reflection spectra of the X-rays of CZTS films, the peaks are observed in planes corresponding to (112), (200), (312) and (008). The intensities of these peaks vary somewhat depending on the annealing temperature and time of sulfurization. The maximum of the main peak (112) corresponds to the sample that underwent annealing at temperatures of 530–550°C for 30 minutes or more.

We investigated the surface morphology and microstructure of the samples. The films were typical of polycrystalline structure. Grain sizes varied within 0.4–1.0 microns. With the increase of the annealing temperature and decrease of cooling rates the grain size increased.

The study of the electrical properties of the films showed that all the films exhibit p-type conductivity. Results support the mechanism of formation of acceptor centers in the CZTS film. The surface resistance of the films varied in the range 10^2–10^4 ohm·□ the heterogeneity of the surface resistance area was about 15%. CVC of p-CZTS /n-Si heterostructures had a pronounced diode character.

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ANALYSIS OF TMGA OUTPUT OF ON-BOARD CYLINDERS FOR CHEMICAL VAPOR DEPOSITION
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The delivery rates of normally liquid or solid MOCVD precursors depend on the temperature of the precursor in its normal phase. For use in the CVD process, the MO precursors are evaporated and transported to the process by use of a carrier gas. The rate of delivery to the process is determined by the vapor pressure. The evaporation process requires heat. Unless this heat is provided continuously through a heater, the precursor will cool and the vapor pressure will drop. For high carrier gas flows and large capacity, short bubblers that are used for epi stack production today, the temperature drop and the associated vapor pressure drop will change considerably over the life of the bubbler as precursor material is depleted. For best control of the process (and highest yield), it is beneficial to have a mathematical expression that predicts the expected output concentration. The mathematical expression uses the carrier gas flow, the precursor level and a geometrical parameter as input to predict the expected concentration shift and the associated correction factor for the carrier gas flow. The mathematical expression uses three constants. We found the value of these constants by fitting the expression to output concentration measurements of cylinders of different shape under various flow conditions.

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GRAIN SIZE OF POLYCRYSTALLINE BA8GA16SN30 TYPE-VIII CLATHRATES GROWN FROM FLUX SOLUTIONS BY VERTICAL BRIDGEMAN TECHNIQUE
Ba$_8$Ga$_{16}$Sn$_6$ type-VIII clathrate is one of the most potential thermoelectric materials for waste heat generators working at around 500 K. In this study, Ba$_8$Ga$_{16}$Sn$_6$ polycrystalline Type-VIII clathrates were grown by means of the vertical Bridgeman technique from BaBa$_{16}$Sn$_6$50 and BaBa$_{16}$Sn$_6$60 flux solutions at various furnace temperatures. Each sample with 10 mm diameter have in the direction of solidification three regions of “multiphase”, “polycrystal” and “Sn flux”. In the polycrystal region, Ba$_8$Ga$_{16}$Sn$_6$30 grains were wetted by an Sn-rich phase. It was found that the temperatures for sample with the largest grain size grown from BaBa$_{16}$Sn$_6$50 and BaBa$_{16}$Sn$_6$60 solutions are 650°C and 600°C respectively, while the grain size for the former is larger. A sample grown at lower temperature has smaller grains. This results from a higher rate of nucleation at a higher undercooling at the solid-liquid interface which is caused by the lower thermal gradient in the liquid. At higher furnace temperatures, enhanced convection in the solution at higher temperature gradients and wetting phenomena may cause instability of the solid-liquid interface, increase nucleation sites and therefore decrease the grain size.

GAINP GRADED BUFFERS FOR 4-JUNCTION METAMORPHIC SOLAR CELLS
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The 4-junction inverted metamorphic solar cell achieves a nearly ideal bandgap combination through the use of compositionally graded buffers. GaInP has been heavily investigated as a material for graded buffers due to its high bandgap, conductivity, and large range of lattice constants. Here, we summarize recent findings about GaInP graded buffers that have enabled access to the subcells required by the 4-junction inverted metamorphic solar cell, and show recent multijunction results.

Graded buffers are known to require structural uniformity: limited composition modulation, precipitates, or other internal defects. In addition to these material properties, we have recently found that atomic ordering in GaInP has a large influence on dislocation behavior. Glide through the ordered planes disrupts the order pattern, creating an anti-phase boundary in the ordering. Using ab initio calculations, we determined that the anti-phase boundary in perfectly CuPt-ordered GaInP has an energy of -9.9 meV/Å$^2$ (Fig. 1a), and so is energetically favorable. This energy is released upon glide and so enhances glide in ordered material. In theory, maximizing ordering while limiting compositional modulation leads to the lowest threading dislocation density from a GaInP graded buffer. However, another consideration is the asymmetry of the CuPt ordered structure. Only half of the typical 60° dislocations produce anti-phase boundaries, resulting in a skewed distribution of dislocations in ordered GaInP buffers. We show how this asymmetry can result in a dislocation formation mechanism when transitioning between ordered and disordered material as the distribution of dislocations changes (Fig. 1b). Using the knowledge of how ordering influences dislocation glide, we create GaInP buffers with 2%/4%/misfit with threading dislocation densities below 1x10$^{10}$ cm$^{-2}$ (4x10$^{10}$ cm$^{-2}$) and 1.0-eV (0.7-eV) GaInAs subcells with Voc above 0.6 V (0.3 V). These subcells have been implemented into a 4-junction metamorphic solar cell with near-ideal bandgaps and efficiency over 45% under concentrated light.

GROWTH AND PYROELECTRIC ENERGY CONVERSION OF PLZST ANTIKERROELECTRIC SINGLE CRYSTAL
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As one of the most attractive candidates for electrical energy storage and pyroelectric energy conversion devices design, La modified complex perovskite antiferroelectric Pb(Zr,Sn,Ti)O$_3$ (PLZST) single crystal, with a morphotropic phase boundary(MPB) composition, had been grown from a modified flux, for its huge remnant polarization P$_r$, and pyroelectric coefficient p alongside an induced AFE- FE phase transition. Bulk PLZST single crystal could be grown from PbO-PbF$_2$-B$_2$O$_3$ complex flux depending on PbF$_2$ evaporation. To learn the influence of phase structure on the polarization and induced phase transition, as-grown single crystal was studied by X-ray diffraction, dielectric and pyroelectric analysis. PLM and TEM results revealed that PLZST single crystal was an antiferroelectric/ferroelectric (AFE/FE) phase coexistence with the AFE phase dominated at room temperature. Temperature-
dependent polarization and strain measurements indicated the AFE phase could be induced into a metastable field-induced FE phase (FEin). The FEin phase could be maintained in the crystal below a critical temperature of 90°C and recovered to AFE phase above it, accompanied with an abrupt field-induced strain of ~0.5% and a higher pyroelectric response. PE loops and pyroelectric analysis indicated that the ferroelectric and pyroelectric properties of PLZST single crystals were both strongly orientation-dependent.

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EMBEDDED SiC NANO-PARTICLES IN Si BY LOW ENERGY CARBON ION IMPLANTATION FOLLOWED BY ANNEALING
Sarah Purdy¹, Michael Bradley, Gap Soo Chang, Andrew Knights²
¹University of Saskatchewan, Saskatoon, SK, Canada, ²McMaster University, Hamilton, ON, Canada

A silicon-based light-emitting material is attractive for photonic applications without the need for bonding of alien materials. The modification of silicon using a common technique would introduce a low-cost, reliable method for large-scale production. In this work, low-energy, high-fluence carbon ion implantation of silicon (C:Si) is used to synthesize a thin film of buried SiC nanoparticles in Si (100). The C:Si is characterized using common techniques: Raman and FTIR spectra indicate that the carbon forms some SiC and carbon clusters after implantation, then SiC with no evidence of C-C bonding after annealing. Grazing incidence X-Ray diffraction shows evidence for polycrystalline SiC and Si after annealing. Transmission Electron Microscopy shows that the thin film consists of multiple layers of polycrystalline and amorphous Si, with a layer of carbon-rich inclusions. Previous work by Wang et al. has shown that this technique for synthesis of SiC on Si is described by the 3-D Avrami equation.

Light-emitting diodes (LEDs) fabricated from the post-anneal C:Si produce red-orange light visible to the naked eye. Gaussian fitting of the electroluminescence spectrum indicates luminescence is associated with emission from porous and amorphous silicon. The use of carbon ion implanted silicon for photonic applications is driven by defects induced by the implantation treatment. However, these defects limit the efficiency of the LEDs.
Materials for Photovoltaics and Energy Technology (Joint ACCGE/OMVPE) 2

Location: Madison
Session Chair(s): John Geisz, Chris Fetzer

7:00 PM - 7:30 PM
III-V NANOWIRES FOR SOLAR CELL APPLICATIONS
Invited
Hoe Tan
The Australian National University, ACT, Australia

Nanowire research is an emerging field growing at a fast pace due to their unique electronic and optical properties. These properties stem from their large surface to volume ratio, high aspect ratio and confinement in two dimensions. Nanowires are of great interest in photovoltaics because of their large surface area and intrinsic antireflection effect that increases light absorption. More importantly, they provide a paradigm shift in photovoltaics by decoupling light absorption from the carrier collection paths, which lead to more efficient charge extraction. By incorporating the superior photovoltaic properties of III-V semiconductors into nanowire structures, it is expected that further enhancement in the solar cell efficiency can be achieved. In addition, material usage in nanowires is much less than in planar devices that will ultimately lead to significant cost reduction. Absorption beyond Beer-Lambert law has led to an overall efficiency of 13.8% in InP nanowire array solar cells [1]. Recently, a very large short-circuit current density, Jsc, of 180 mA/cm² and an ‘apparent’ efficiency of 40% was achieved for a solar cell based on single vertical GaAs nanowire [2].

In this talk, I will present an overview of nanowire photovoltaic activities at the Australian National University. Our design work shows that nanowires act as selective spectral concentrators. This behaviour is very different to ‘normal’ concentration used for planar solar cells and leads losses which are dependent on the structural parameters of the nanowires. The ultimate efficiency is not just a function of the bandgap of the absorber but also the structural parameters of the nanowires. Our experimental effort focuses on the growth of InP and GaAs-based nanowires by both the vapor-liquid-solid mechanism and selective area growth. The optical and structural properties of the nanowires will be presented. Various issues with such as tapering, compositional non-uniformity along nanowires, crystal structure and carrier lifetime will be discussed. We show that surface passivation is a main issue in the case of GaAs-based nanowires but not in InP-based nanowires, due to the difference in surface recombination velocity. In addition, we will show that junction position is also an important consideration to maximize the efficiency of the device.


7:30 PM - 7:50 PM
MOVPE-GROWN INGAP SOLAR CELL ON GE-ON-SI VIRTUAL SUBSTRATE
TAEWAN KIM, Brian Albert, Brian Pearson, Lionel C. Kimerling, Jurgen Michel
Massachusetts Institute of Technology, Cambridge, MA

Novel approaches of solar power conversion include both photovoltaic and solar thermal for high efficiency power generation and dispatchability by splitting the solar spectrum to generate electricity in the PV part and storage by using thermal receivers. This approach has the advantage that high efficiency photovoltaic cells, operating near the bandgap of the material, can be used. InGaP, lattice-matched to a Ge-on-Si substrate, not only provides a wide band gap (Eg ~ 1.9 eV) but also utilized a low cost substrate and is therefore an excellent candidate for this approach. InGaP single junction solar cells grown by metalorganic vapor phase epitaxy (MOVPE) on Ge-on-Si virtual substrates were investigated. A Si substrate provides several advantages such as higher thermal conductivity, mechanical robustness, and low-cost, compared to typically used Ge or III-V substrates. In an attempt to achieve high solar cell performance, the threading dislocation densities (TDD) of the lattice mismatched materials have to be restricted to about 10⁶ cm⁻². High quality InGaP films on Ge-on-Si virtual substrates, associated with a long minority carrier lifetime, are sensitive to both good heteroepitaxy at the InGaP/Ge and at the Ge/Si interface. High quality Ge-on-Si heteroepitaxy is challenging due to the large lattice-mismatch (4.2 %). There are two possible implementations of Ge-on-Si substrates. One method is based on a SiGe graded buffer, which can achieve sufficiently low TDDs for photovoltaic applications, but requires a thickness of over 10 μm and exhibits a strain related cross hatch. An alternative method employs a two-step selective area epitaxial Ge growth followed by cyclic thermal annealing, resulting in thin films with specular surface. Prior studies indicate that Ge-on-Si heteroepitaxy using ultra-high vacuum chemical vapor deposition (UHV-CVD) employing two-step growth and cyclic thermal anneal procedures for high quality Ge film yield TDDs of 2×10⁶ cm⁻² for blanket Ge films and 2×10⁵ cm⁻² for Ge films selectively grown inside silicon dioxide trenches. Here we present an InGaP solar cell structure without anti-reflection coating that was grown on a Ge substrate, exhibiting 11.7 mA/cm² short circuit current, 1.26 V open circuit voltage, and a 75.2 % fill factor under 0.5 sun. Note that the efficiency of the InGaP solar cell on the Ge substrate at room temperature for a 1.9 - 2.4 eV wavelength range, selected for direct power conversion, is over 50 %. We will present InGaP solar cells on Ge-on-Si substrates as well.

7:50 PM - 8:10 PM
INVERTED METAMORPHIC TANDEM DEVICES FOR EFFICIENT PHOTOELECTROCHEMICAL WATER SPLITTING
Henning Döschner¹, Ryan M. France², James L. Young², Todd G. Deutsch², John F. Geisz², John A. Turner²
¹National Renewable Energy Laboratory (as well as Philipps-Universität Marburg and Technische Universität Ilmenau), Golden, CO,
²National Renewable Energy Laboratory, Golden, CO
Solar fuel generation by direct photolytic splitting of water is a pathway towards energy storage and transportation demands in a sustainable energy economy. High band gap semiconductor materials may drive the water splitting reaction, but neglect substantial parts of the solar spectrum, while common photovoltaic (PV) absorbers fail to provide sufficient threshold voltage. Tandem absorber structures overcome this undesirable trade-off featuring promising efficiency potentials [1], and high-efficiency PV inspired epitaxial GaInP2/GaAs photoelectrodes [2] enabled world record solar to hydrogen (STH) conversion efficiencies of up to 12.4% [3]. Although the optimum band gaps for highest STH efficiency was discussed for decades, the impact of sunlight absorption during illumination through an aqueous electrolyte have been neglected until recently [1]. We discussed the loss of solar photon flux during transmission through water, applied a detailed balance approach to derive STH efficiency prospects, discovered a PEC design principle relating electrolyte thickness and allowable overvoltage loss, and derived optimum band gap combinations for water splitting tandem structures (Fig.1).

In contrast to the maximum power metric in PV, optimum STH efficiency requires a maximum current at sufficient potential, i.e., 1.23V thermodynamic water splitting potential plus system losses consolidated in an overvoltage term. Detailed balance calculations predict ideal band gap combinations [1], but materials availability strictly limits realization. Inverted and metamorphic III-V growth and processing techniques have been developed to advance high-efficiency PV [4]. We transferred these concepts to PEC application; defined desirable tandem structures with new band gap combinations and transparency conditions for step graded buffers; and demonstrated unassisted water splitting (Fig.2a). Preliminary results indicated STH efficiencies of 15% and above (Fig.2b), with a pathway towards advanced tandem PEC devices with specifically adjusted band gaps boosting the prospects to 22% (Fig.1) and beyond.

![Fig.1 - Detailed balance limiting STH efficiency of tandem PEC devices illuminated through 1cm electrolyte and operated at a total](image-url)
of 1050mV of overvoltage loss.

Fig.2 - Current-voltage (I-V) characteristics of advanced PEC devices: (a) laboratory based measurements of triple (blue) and double (red) junction proof-of-principle structures, (b) efficiency estimate based on outdoor measurements (sunlight illumination).

References

8:20 PM - 8:40 PM
MOVPE GROWTH OF HIGH EFFICIENCY INVERTED METAMORPHIC 4-JUNCTION SOLAR CELLS
Xingquan Liu, Eric Rehder, Joseph Boisvert, Christopher Fetzer, Daniel Law, Shoghig Mesropian
Boeing Spectrolab Inc., sylmar, CA

Inverted metamorphic multiple junction (IMM) solar cells have attracted attention due to the advanced structure design to achieve high efficiency. Based on IMM 3-junction development experience in Boeing Spectrolab, IMM 4-junction solar cells have been under development using Veeco K475 metalorganic vapor phase epitaxy (MOVPE) tool. IMM 4-junction with subcell combination as AlGaNp/AlGaAs/GaInAs/GaInAs (lower bandgap) was grown on 100mm diameter GaAs substrate in inverted configuration with the sunward toward to substrate. Metamorphic step graded buffer layers were grown before subcell-3 to relax most of the strain caused by the lattice mismatch between subcell-3 and substrate. On top of subcell3, second step graded buffer layers were grown to further increase the lattice constant to subcell4. Figure 1 shows the schematic diagram of the IMM 4-junction structure. XRD reciprocal space mapping (RSM) was accomplished using a Philips MRD system. The RSM shows the strain is mostly relaxed for both subcell3 and subcell4. AlGaNp cell bandgap and growth rate uniformity has been tuned to achieve high performance large area solar cells. Photoluminescence (PL) mapping was used to characterize the bandgap uniformity. Figure 2 shows the PL mapping of bandgap and intensity across a 100mm diameter wafer. The bandgap range is within 12meV. The device structure was then transferred to a handle wafer and processed into solar cells. The anti-reflectance film was coated to reduce the sunlight reflection. The illuminated current-voltage (LIV) characteristics were taken on the IMM 4-junction devices under 1x AM0 using Spectrolab’s AX25 solar simulator and demonstrated 34.1% efficiency.

This project is supported by the Air force Research Laboratory under contract FA8650-12-5501.

Figure 1 Schematic Diagram of IMM 4-junction Solar Cell.
Figure 2 AlGaNp AlGaNp subcell PL map. The bandgap range within 12meV across wafer.
The optical properties of GaAs$_{1-x}$Bi$_x$ have been reported to be sensitive to post-growth thermal annealing [1]. Here, we report the OMVPE growth and characteristics of (Al$_x$)Ga$_{1-x}$As/GaAs$_{1-y}$Bi$_y$, and the strain-compensated GaAs$_x$P$_{1-x}$/GaAs$_{1-y}$Bi$_y$ heterostructures for photovoltaic applications. In-situ thermal annealing under argon over-pressure is shown to improve the luminescence properties of these material systems. Single-junction solar cells employing GaAs$_{1-y}$Bi$_y$ are used to further characterize the impact of thermal annealing.

Two samples for annealing studies, 3 period Al$_{0.1}$Ga$_{0.86}$As/GaAs$_{0.965}$Bi$_{0.035}$ (12nm/15nm) and 3 period GaAs$_{0.1}$P$_{0.9}$/GaAs$_{0.96}$Bi$_{0.04}$ (20nm/21nm), were grown by OMVPE on (100) semi-insulating GaAs substrates. The GaAs$_1$Bi$_y$ was grown by the simultaneous feed of TEGa, TEBi, and TBAs at 420℃. The samples were annealed at various temperatures under argon ambient for 40min. Room Temperature Photoluminescence (RT-PL) measurements were performed to find the optimal annealing condition and XRD measurements to detect any structural change in the samples. Single-junction solar cell structures employing 5 period GaAs$_{0.1}$Bi$_{0.9}$/GaAs (33nm/20nm) were also grown and subjected to annealing at either 650℃ or 700℃ during the growth of the emitter, the window, and capping layers above the base region. Both annealing study samples with either Al$_{0.1}$Ga$_{0.86}$As or GaAs$_{0.1}$P$_{0.9}$ barriers annealed at 650℃ for 40min exhibited a 9-11-fold increases in PL intensity at room temperature compared to that of their as-grown material, with the peak position around 1.06μm (Fig. 1.a). The $\omega$2θXRD patterns indicate little change after annealing, although higher temperature annealing diminishes the XRD fringe contrast (Fig. 1.b). Annealing studies on MBE-grown dilute-bismide material employing RTA under nitrogen indicated an optimal temperature 500℃ for 1 min, resulting in a 2 fold increase in PL intensity [2]. The XRD measurements on the solar cell samples reveal that the sample whose upper layers were grown at 700℃ exhibits diminished fringe contrast, possibly resulting from interdiffusion of the interfaces. Initial device results from the unoptimized (700℃ annealed) solar cell material demonstrate an extended EQE spectral response up to 1.09eV and a conversion efficiency of 1.07%.

In conclusion, (Al$_x$)Ga$_{1-x}$As/GaAs$_{1-y}$Bi$_y$ heterostructures were grown by OMVPE, and in-situ annealing was performed to improve their luminescence properties. Based on these annealing studies, solar cell structures were grown and characterized.


![Fig 1.](image)

(a) PL from 3x GaAs$_{0.9}$P$_{0.1}$/GaAs$_{0.96}$Bi$_{0.035}$ structure annealed at various temperatures

(b) HR-XRD (004) Pattern of 3x GaAs$_{0.9}$P$_{0.1}$/GaAs$_{0.96}$Bi$_{0.035}$ structure
regarding ongoing efforts to synthesize nanocrystalline or amorphous nitride alloys that could ultimately enable high-performance, low-cost photovoltaic devices
8:00 AM - 10:00 AM

Materials for Photovoltaics and Energy Technology (Joint ACCGE/OMVPE) 3

Location: Gallatin
Session Chair(s): Ted Ciszek, Jeff Derby

8:00 AM - 8:30 AM
ON THE POTENTIAL AND LIMITS OF LARGE AREA SEEDING FOR PHOTOVOLTAIC SILICON
Invited
Nathan Stoddard
SolarWorld Americas, Hillsboro, OR

Single crystal production of silicon for solar cell substrates has relied on the Dash neck technique developed more than 50 years ago. The technique is simple and repeatable and enables truly dislocation free crystal growth. It does have drawbacks, however, including limits on throughput and some structural difficulties. It has long been assumed that dislocation-free growth is not possible by any other method. In the ‘quasi-mono’ crystal growth technique, one of the key elements is the use of large area single crystal seeds. By melting the seeds at near-equilibrium conditions, it is feasible to avoid the production of dislocations during melting. We will review the dislocation relevant details of the large area seeding process and present best case results for dislocation density, including measured minority carrier lifetimes in excess of 1 ms on p-type material. We will focus on dislocation density exclusive of seed boundaries, but we will also present a potential best-case limit for the technique.

8:30 AM - 8:50 AM
NUMERICAL MODELING OF A KYROPOULOS PROCESS TO GROW QUASI SQUARE SILICON INGOTS FOR PHOTOVOLTAIC APPLICATIONS
Ahmed NOURI*, Leslie Lhomond†, Guy Chichignoud†, Yves Delannoy†, Bachir Helfia†, Ibn Khaldoun Lefkaier*, Kader Zaidat†
1Grenoble University Alpes, CNRS-SiMaP laboratory, st Martin d'Heres Cedex, France, 2Laghouat University, LPM Laboratory, Laghouat, Algeria

The Kyropoulos crystal growth technique offers several advantages that could be beneficial for the production of photovoltaic silicon: an expected low dislocation density thanks to lower thermal gradients, and a square shaped ingots to improve material yield. In our work, we simulate a Kyropoulos process to grow square silicon ingots. The studied furnace is a modified DSS furnace with three heating zones operating as a Kyropoulos machine for silicon with a square crucible. Experimental and numerical investigations are lead in parallel to feed on each other and improve our understanding of the growth conditions. Due to the square geometry, 3D modeling was carried out to study temperature distribution as well as fluid dynamics and solidification. The model highlights and explains some unexpected phenomena observed in our experiment. We have identified that the initial geometry and process parameters lead to an ascendant central hot melt flow creating a hot central zone in the melt, which is detrimental for growing silicon from the seed. A solution to this problem was proposed, simulated and implemented experimentally. The obtained experimental results were as predicted by our simulation model. The new proposed geometry allows the establishment of a cold zone in the desired area around the seed, allowing favourable temperature conditions for the lateral growth from the seed. The obtained experimental results were as predicted by our simulation model and a silicon crystal was successfully grown using this improved configuration.

8:50 AM - 9:10 AM
PHOTOVOLTAIC SI INGOTS IN COMPARISON WITH MONOLIKE SI AND HIGH-PERFORMANCE MULTICRYSTALLINE SI
Kentaro Kutskakke, Momoko Deura, Yutaka Ohno, Ichiro Yonenaga
Tohoku University, Sendai, Japan

Monolike (ml-) Si and high performance multicrystalline (HPmc-) Si have been extensively studied as a Si ingot in the next generation for solar cell applications. The former is a quasi-monocrystalline Si grown using single-crystalline seeds tiled on the bottom of a crucible. The latter is a small grain mc-Si ingot grown on incubation Si seeds with fine grains. Both methods are based on conventional growth method for mc-Si ingots, and consist of almost the same growth procedures: melting raw Si materials with keeping the seeds as solid, directional solidification on the seeds, and cooling down to RT. Although both growth methods are desirable, comparison of the structural and electrical characteristics of these Si is essential. Here, we grew ml- and HPmc-Si ingots using the same furnace and the similar growth recipe to compare grain structure and distribution of carrier lifetime in the ingots. The ml-Si showed almost similar carrier lifetime with the HPmc-Si. Observed number of dislocation clusters detected by PL imaging in the HPmc-Si was slightly higher than that in the ml-Si, much smaller than that in the conventional mc-Si. These difference would reflect material features caused by the difference of the seed. Though the present result cannot make an answer to the question which ml- or HPmc-Si is more suitable material for solar cells, it was clearly indicated that both type Si have a superior of low density of defects in comparison with conventional mc-Si, suggesting that mono-like Si and HPmc-Si have a potential to be major in the casting method for the next generation solar cells.

9:10 AM - 9:30 AM
CONCENTRATION AND LOCALIZATION OF IMPURITIES IN SILICON BY COLD-CONTAINER CRYSTAL GROWTH FOR ENHANCED ANALYTICAL DETECTION
Ted F. Ciszek
Siliconsultant Division of Geolite, Evergreen, CO
Even at $< 1 \times 10^{15}$ atoms/cm$^3$ concentration levels, some impurities in silicon have a detrimental effect on the performance of photovoltaic devices, detectors, and other minority charge carrier lifetime dependent device structures. Impurity detection at such low levels can be problematic. Inductively-coupled cold containers (cold crucible or cold boat) were used to melt and re-solidify silicon samples of various shapes so that impurities are concentrated into a small, localized region for easier detection. Electromagnetic forces substantially isolate the melt from the crucible or boat walls and facilitate a well-controlled last-to-freeze region where impurities in the sample are concentrated by their small segregation coefficients. The figure below illustrates an example in which ~30g of polycrystalline silicon feedstock chunks in a cold copper boat (top) is zone-solidified at 2.5mm/min with a ~3cm zone length (lower left), and the last-to-freeze melt is electromagnetically levitated as it freezes (lower right).

For an ingot $N$ zone lengths long, impurity concentration $C(x)$ vs. position $x$ along the ingot (where $x$ is in zone lengths) is given, to first order, by $C(x)/C_0 = 1 - (1-k)x$ for $0 < x < (N-1)$, and by $C(x) = C(N-1)(N-x)^{-k}$ for $(N-1) < x < N$. $N$ is ~6 in this experiment. $C_0$ is the original concentration in the feedstock chunks (assumed uniform) for an impurity with effective segregation coefficient $k$. By evaluating the integral of $C(x)$ vs. $x$ very near the last-to-freeze tip, it is shown that over 99% of an impurity with $k < 1 \times 10^{-4}$ is concentrated in the last 1/300th of the ingot to freeze. So a ~0.1g sample can be removed from the last-to-freeze tip for impurity analysis by techniques such as inductively-coupled plasma mass spectroscopy. When impurity concentrations in the ~0.1g enriched region are related back to the ~30g original sample, an approximately 300X improvement in detection limit is acquired for such impurities. Most detrimental metallic impurities in silicon have $k < 1 \times 10^{-4}$.

With the cold container approach for concentrating impurities there is no cylindrical-rod or granular sample geometry restriction as with float-zone impurity concentration techniques. Also, there is no obfuscating impurity introduction from quartz crucibles or graphite hot zones.

THREE-DIMENSIONAL ANALYSIS OF DISLOCATION MULTIPLICATION IN SINGLE-CRYSTAL SILICON UNDER ACCURATE CONTROL OF COOLING HISTORY OF TEMPERATURE

Invited
Bing Gao, Satoshi Nakano, Koichi Kakimoto
Kyushu University, Fukuoka, Japan

The photovoltaic industry is in a phase of rapid growth, and has increased by over 44% per year over recent years. Two of the main challenges of today’s photovoltaic industry are cost reduction and the increase of solar cell efficiencies. Solar cell efficiencies can be affected by many factors, such as impurities, point defects, grain boundaries, and dislocations. Dislocations have been identified as one of the most efficiency-relevant defect centers in crystalline silicon for photovoltaic devices. The requirement for an increase of solar cell efficiencies necessitates a reduction of dislocations.

In crystalline silicon, dislocations usually take place in the high-temperature processes of crystal growth, such as crystallization and cooling processes. The crystallization process usually contributes slightly to the increase of dislocations, whereas the cooling process has a large effect on the increase of dislocations. Hence, many studies have concentrated on the cooling process. However, the results are not consistent. Slow cooling was suggested for obtaining low dislocation density in GaP/Si heterostructures and in SiGe layers grown by liquid phase epitaxy. Fast cooling was suggested for obtaining low dislocation density in Pb and Si crystal growth from the melt. This discrepancy shows that the effect of the cooling process on the multiplication of dislocation is complex and different for different materials, growth furnaces, and growth processes. To better understand the relationship between the cooling rate and dislocation, it is essential to study the effect of the cooling process on the increase of dislocations from the perspective of accurate control of temperature history inside furnace according to a pre-designed curve.

To obtain accurate temperature control, a numerical solver, which simulates the automatic control process, such as proportional-integral-differential (PID) control process, has been developed. To simulate dislocation multiplication, an advanced 3D model, which includes the immobilization of mobile dislocations, the jog formation between different slip systems, and the short-range internal...
stress influence from the total dislocation density, was developed. We used those solver and model to study the effect of cooling process on dislocation multiplication, and attempt to clarify the following problem: what is the most effective method to reduce dislocations when the cooling process is designed?

Acknowledgements
This work was partly supported by the New Energy and Industrial Technology Development Organization under the Ministry of Economy, Trade and Industry (METI), Japan.
Nonlinear Optical and Laser Host Materials (ACCGE) 3

Location: Madison
Session Chair(s): Shekhar Guha

8:00 AM - 10:00 AM

Wednesday, August 5, 2015

SINGLE-CRYSTAL FIBER OPTICS-A REVIEW
Invited
James A. Harrington
Rutgers University, Piscataway, NJ

Single-crystal (SC) fiber optics made from oxide crystals such as sapphire and YAG have promising applications as both passive and active fibers. Most SC fibers such as sapphire are transmissive up to about 3 μm and, therefore, are potentially excellent fibers for the transmission of high-power Er:YAG lasers operating near 3 μm. As an active fiber, SC fibers grown from rare-earth doped YAG and other garnets could provide an excellent alternative to conventional glass fiber lasers and amplifiers for the generation of extremely high laser powers. In general, the optical and physical properties of SC fibers, including reduced non-linear effects such as stimulated Brillouin scattering (SBS) and high thermal conductivity, often exceed those of glass fiber optics. The methods to grow SC oxide fibers, which include laser heated pedestal growth (LHPG), will be reviewed along with their optical and laser properties.

8:45 AM - 9:00 AM
ADVANCES IN CRYSTAL GROWTH AND CHARACTERIZATION OF SINGLE CRYSTAL CdSiP2
Kevin T. Zawilski1, Peter G. Schunemann1, F. Kenneth Hopkins1, Shekhar Guha1, Jon Slagle2, Joel Murray2, Jacob Barnes2, David E. Zelmon3, Steve Fenstermaker3
1US Air Force Research Laboratory, Wright-Patterson AFB, OH, 2University of Dayton Research Institute, Dayton, OH

CdSiP2 (CSP) is a high temperature analog to ZnGeP2 (ZGP) with a larger bandgap and promising characteristics for IR frequency conversion. Crystals are birefringent and are transparent from 0.5 to 9 microns. The non-linear coefficient (d36) of CSP has been measured to be 85 pm/V, making this the highest non-linear coefficient for any 1 micron pumped NLO crystal. Recent developments in the growth of single crystals using the horizontal gradient freeze (HGF) technique in high-temperature transparent furnaces from a stoichiometric melt, including scaling of growth size and use of free-standing PBN boats, are discussed. While cracking and twinning of the crystals continue to be the major problems during growth, high optical quality, crack- and twin-free single crystals were grown through this method. Chemical analysis of inclusions found in some crystals was used to better understand the growth process. Measurements of the electro-optic coefficient were taken for the first time. Crystal samples with no near IR absorption and laser polished surfaces were tested for laser damage threshold. Recent results from several frequency conversion laser experiments are also given.

9:00 AM - 9:15 AM
IDENTIFICATION OF NATIVE DEFECTS IN CdSiP2 CRYSTALS USING ELECTRON PARAMAGNETIC RESONANCE
Eric M. Golden1, Ember Maniego1, Nancy C. Giles1, Larry E. Halliburton1, F. Kenneth Hopkins1, Peter G. Schunemann1, Kevin T. Zawilski1
1Air Force Institute of Technology, Wright-Patterson Air Force Base, OH, 2University of Dayton Research Institute, Dayton, WV, 3Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, 4BAE Systems, Nashua, NH

Single crystals of CdSiP2 are presently being grown at BAE Systems for use in frequency conversion applications in the mid-infrared. Native defects are present in these crystals and are identified using electron spin resonance (EPR). The spectrometer operates near 9.5 GHz and spectra are obtained in the 5-40 K temperature range. Illuminating a CdSiP2 crystal at low temperature with a He-Ne laser (633 nm) changes the charge states of the native defects as electrons are “pumped” from acceptors to donors. This converts the defects into paramagnetic states and allows their presence to be easily detected with EPR. Thus far, EPR spectra from two acceptors (cadmium vacancies and silicon vacancies) and one donor (silicon-on-cadmium antisites) have been identified. In each case, unique hyperfine interactions with neighboring phosphorus ions provide the critical information to make the identifications. The singly ionized cadmium vacancy shows equal hyperfine interactions of 50 G with only two of its neighboring
phosphorus nuclei. In contrast, the singly ionized silicon vacancy shows equal hyperfine interactions of 41 G with all four of its neighboring phosphorus nuclei. This different behavior for the two vacancies is a reflection of the much smaller size of the missing silicon ion (0.26 Å radius) relative to the missing cadmium ion (0.78 Å radius). When a silicon ion replaces a cadmium ion, the resulting EPR-active doubly ionized charge state of this antisite donor can be photoinduced and has equal hyperfine interactions of 195 G with only two neighboring phosphorus nuclei. This much larger hyperfine interaction is expected for a donor centered at a cation site, and the small size of the silicon ion is responsible for the interaction with only two neighbors. The position of the Fermi level is found to vary from sample to sample, and depends on the relative concentrations of native defects and Fe impurities. A major goal of these defect studies is to correlate specific defects with unwanted near- and mid-infrared absorption bands.

9:15 AM - 9:30 AM
BULK GROWTH ON SODIUM TETRABORATE DECAHYDRATE SINGLE AND INVESTIGATIONS ON THEIR THERMAL AND OPTICAL PROPERTIES
Ezhil Vizhi R, Lakshmipriya M
VIT University, Vellore, India

Borate materials have been extensively studied because they show a great variety of physical properties ranging from nonlinear optical (NLO), ferroelectric to semiconducting behaviors and in addition, a boron atom may adopt triangular or tetrahedral oxygen coordination, the BO3 and BO4 groups may be further linked via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, leading to the rich structural chemistry. By considering the above mentioned advantages, Sodium tetraborate decahydrate single crystal was selected for current investigation. Nucleation and growth kinetics give valuable information about the crystal growth process, which can be utilized in the growth of large size crystals. By gravimetric analysis, the solubility of Sodium tetraborate decahydrate was analyzed, it exhibits positive temperature coefficient of solubility. The grown crystal exhibits a wider zonewidth at higher temperature, which may be the optimized condition to grow bulk single crystal. Further, in order to find out the optimized the degree of supersaturation to control the spurious nucleation induction period was studied by isothermal method over the equilibrium temperature range by varying the degree of supersaturation. By following the classical theory of nucleation, the critical parameters involved in nucleation such as Gibbs critical free energy, interfacial energy, radius of critical nuclei, nucleation rate and number of molecules present in a critical nucleus was estimated. Bulk single crystal of Sodium tetraborate decahydrate grown by slow cooling technique. Structural analysis shows that the crystal belongs to monoclinic system with space group C2/c. Thermal stability of the crystal was analyzed by TGA/DTG. The existence of SHG was confirmed by Q-switched Nd-Yag laser technique. The essential requirements for a nonlinear optical crystal are a very good transmittances and lower cutoff wavelength. Hence, UV-Vis-NIR spectrum was recorded over a wavelength of 200-900 nm and its cutoff wavelength was determined as 221 nm. The crystals possess maximum absorption in the ultraviolet region and maximum transmittance in the visible region which is the most desirable property of a NLO material for device fabrication. The band gap (Eg) and other optical constants such as reflectance, extinction coefficients were estimated from the UV-Vis-NIR data. SHG of the material is found to be 4 times that of KDP.

Reference
GROWTH OF N-BENZYL-2-METHYL-4-NITROANILINE (BNA) SINGLE CRYSTAL FIBER FOR TERAHERTZ GENERATION.

Kei Kamada\textsuperscript{1}, Yuma Takida\textsuperscript{2}, Hiroaki Minamide\textsuperscript{2}, Shunsuke Kurosawa\textsuperscript{1}, Yuui Yokota\textsuperscript{1}, Yuji Ohashi\textsuperscript{1}, Akira Yoshikawa\textsuperscript{1}

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Technology using terahertz (THz) region has recently been developed [1], and THz generation and detection technique attracts interest for many application fields, such as biomedical imaging, security, medicine, art conservation, and nondestructive testing [2]. A monochromatic THz-wave source using a nonlinear optical (NLO) process was employed in developing many of these applications, but the advancement of broadband sources and sources that possess some degree of frequency agility is desirable. In the developments on THz-wave technology, recently difference-frequency generation (DFG) was reported about its great advantage of ultra-broadband capability using the organic solid N-benzyl-2-methyl-4-nitroaniline (BNA) [3]. BNA, which was invented by Hashimoto, is a promising material for wideband, efficient, and high-power THz-wave generation because of its large second-order optical nonlinearity. The BNA-DFG monochromatic THz-wave was tunable over the range 0.1-15 THz. In order to improve efficiency of generating THz-wave and to realize position sensitive parallel THz-wave generation and detection system, BNA thin fiber single crystal was required to directly couple with optical fiber line in DFG system. In this report, BNA thin fiber single crystals were grown by micro pulling down method. Crucible materials and shape were designed according to wetness between BNA and the crucible materials. Finally BNA fiber single crystal with about 1mm diameter was successfully grown (fig.1). In my presentation, design of growth furnace and insulators, crystal structure and x-ray locking measurement results will be reported. Figure 1, BNA fiber single crystal grown by micro pulling down method


GROWTH, THERMAL AND SPECTROSCOPIC PROPERTIES OF A YTTERBIUM DOPED LASER CRYSTAL
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A high-quality disordered Yb³⁺:Ca₃Lu₂(BO₃)₄ laser crystal was grown by the Czochralski method. The thermal properties, including the average linear thermal expansion coefficient, thermal diffusivity, specific heat, and thermal conductivity were systematically measured for the first time. The polarized spectral properties of the crystal were investigated, including the polarized absorption spectra, polarized fluorescence spectra, and fluorescence decay. All of these properties show that Yb³⁺:Ca₃Lu₂(BO₃)₄ is a promising disordered crystalline laser material.
The impact of the buffer layer and substrate surface restructuring on the graphene thickness evolution of larger area SiC substrates has not been studied in detail. The aim of the present work is a deep understanding of the role of buffer layer and growth parameters for having a full control on the epitaxial graphene growth process on SiC to obtain cm scale continuous coverage of ML graphene. During the graphene growth process on the Si-face of SiC the first grown carbon layer, is covalently bonded to the SiC substrate. This so-called buffer layer lacks the πbands of graphene and only the second carbon layer (known as monolayer graphene (ML)) shows the properties of graphene. The buffer layer is a precursor for graphene formation and can strongly influence its quality; depending on the buffer layer integrity the graphene may contain defects. We also study surface futures such as adsorbrates on the graphene layers to improve the graphene quality.

Graphene samples were grown on the Si face of different SiC polytypes in an inductively heated furnace at a temperature ranging from 1700 - 1950°C and at argon ambient with a pressure range from 750 - 950 mbar at different growth times. Graphene surface morphology, thickness, structure and defects have been assessed by using AFM in different modes, LEEM, Raman spectroscopy and reflectance mapping.

It was observed that formation of the buffer layer can start from any place on the substrate, but preferable place is the bending part of the step edge. Graphene formation was analyzed in respect to step bunching and surface decomposition energy differences created by the SiC basal plane stacking sequence on different SiC polytypes. AFM results in the present work demonstrated that the completion of the buffer layer halts step bunching process, which means the surface energy becomes uniform all over the substrate surface after coverage by a buffer layer. It is shown that before buffer layer is completed the step height increases linearly and after that the step height is roughly constant, which means no more step bunching occurs.

The results from graphene samples grown at different argon ambient pressure prove that there is an optimal argon pressure yielding a large coverage of ML graphene. This indicates that at too high argon pressure the Si sublimation is suppressed by bombardment with argon atoms which decreases the graphene growth rate.

Due to the weak electron-phonon coupling and strong electron-electron interaction in graphene, the photothermoelectric effect provides a highly sensitive detection mechanism for electromagnetic radiations absorbed in the electronic system. We present here a bi-metal contacted graphene thermoelectric THz photodetector with sensitivity exceeding 700 V/W at room temperature and noise equivalent power less than 20 pW/Hz1/2, competitive with the existing THz technology, while time-resolved measurements indicate our graphene detector is eight to nine orders of magnitude faster. We further present a large area terahertz detector that utilizes a plasmonic resonance in sub-wavelength graphene micro-ribbons on SiC to increase the absorption efficiency and thus enhance the optical responsivity of the detector. Through Fourier transform infrared spectroscopy we show that by tailoring the orientation of the graphene ribbons with respect to an array of sub-wavelength bimetallic electrodes, the plasmonic resonance can be efficiently excited, with a gate-tunable resonance frequency in the terahertz range. Polarization-dependent photoresponse measurements show an enhanced photothermal voltage between the outermost electrodes due to the plasmonically enhanced absorption.
breaking the device’s symmetry, a net current is produced through the diffusion of hot-electrons. Asymmetric devices are created using dissimilar metal electrodes or electrostatic gating, the latter is the approach used in this work. We fabricated our detectors for photothermoelectric operation on epitaxial graphene using lift off resist in an improved lithography process that results in greatly reduced surface contamination and yields low contact resistance. The epitaxial graphene was formed on nominally on-axis, semiinsulating (0001)6H-SiC via Si sublimation under Ar ambient at temperatures near 1580°C. The field effect transistors (FETs) are constructed with a high-κ hafnium dioxide gate dielectric deposited by atomic layer deposition using a XeF2 seeded surface where the top gate metal was a thin, ≈10nm, asymmetric nichrome (NiCr) that facilitates tuning the photovoltaic response. The NiCr gate possesses a sheet resistance of ≈990ohms which enables better matching to free space and hence does not appreciably attenuate the incoming THz radiation. While the detectors are designed for THz operation they also demonstrate a clear response to 633nm incident radiation. We report results on some of these FETs as a function of gate bias and wavelength.

This work was sponsored by the Office of Naval Research

GROWTH OF HIGH MOBILITY EPITAXIAL GRAPHENE VIA SYSTEMATIC HYDROGEN INTERCALATION FOR THZ PLASMONICS

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Graphene, with such properties as high electrical and thermal conductivity, large room temperature mobility (>200,000cm2/Vs), and low electronic noise, is seen as a promising plasmonic material, offering improvements over metal for surface plasmon polariton (SPP) formation with larger shrinkages of light, tighter SPP confinement and theoretically longer propagation lengths at ~200 wavelengths. Tunability by doping and electrostatic gating are seen as superior properties compared to metals, where graphene devices are capable of working in multiple frequency ranges into THz regime. Epitaxial growth of graphene via sublimation of silicon and graphitization of carbon atoms of silicon carbide (SiC) is ideal for large scale manufacturing of plasmonic devices but due to partially covalent bonding between the SiC (0001) substrate and the first carbon layer (√6 buffer layer), the high room temperature mobility necessary for THz plasmonics is reduced to ~1000cm2/Vs. The objective of this work is to improve THz response of EG by increasing the mobility and carrier concentration of graphene through hydrogen intercalation where the Si atoms covalently bound to the buffer layer are satisfied by hydrogen atoms and create quasi free standing graphene.

Graphene was grown from 6H-SiC (0001) in an Aixtron/Epigress VP508 horizontal hot-wall reactor. SiC was etched in H2 during temperature ramp to 1570°C and graphene was grown at 1580°C for 20 min in Ar ambient. H-intercalation of EG was carried out in the same reactor at 1050°C with a flow of 80slm of H2 and chamber pressure of 900mbar for 30-60 minutes. From SEM we observe the degree of hydrogen intercalation where at 30 minutes some terraces remain coupled to the SiC substrate with mobility ~2250cm2/Vs via Hall. At 45 and 60 minutes the buffer layer becomes mostly quasi free standing with small spots possibly coupled to the substrate as observed in the SEM with mobilities of ~3300 and ~4000cm2/Vs respectively. Raman spectroscopy using a 532nm laser (9.6mW) and spot size of 0.3μm were used to take 80x10μm2 maps of each sample where release of the buffer layer is as evident by the broadening of the 2D peak full-width-half-max (FWHM) before and after H-intercalation. Mobility and morphology optimization correlated by Hall, XPS, Raman and SEM are ongoing. Measurements of the resulting THz transmission spectra are underway to determine if the increase in mobility and carrier concentration results in narrower THz response.
Using an ion beam assisted deposition (IBAD) texturing process we are able to create biaxially aligned films as templates for GaN epitaxy. We are developing the IBAD process to produce low-cost, flexible metal substrates as potential alternatives to sapphire and silicon for electronic devices. Results regarding MOCVD GaN epitaxy on our engineered substrates will be presented. We have achieved GaN films of several microns on polycrystalline metal foils that have in-plane and out-of-plane alignment of less than 1° FWHM.

CdS, ZnS and mixed (Cd,Zn)S nanocrystals were epitaxially nucleated on polymerized 10,12-pentacosadiynoic acid, polydiacetylene (PDA) Langmuir films. The crystals were crystallographically oriented with respect to the template film. ZnS (zincblende structure) was nucleated from the (001) plane with an approximate match to the PDA film in a particular orientation. Accumulated mismatch of the crystals with the underlying template caused growth cessation on the template, resulting in formation of twinning defects on the {111} planes. CdS, that in ambient conditions forms hexagonal wurtzite crystals, was nucleated on the PDA template in the cubic zincblende structure from the (001) planes, similarly to ZnS. However, upon mismatch accumulation with the PDA template, growth on the template is hindered, resulting in transformation to the zincblende structure by the formation of stacking faults on the {111} planes, ( (00.1)_w ). The composition of solid solution (Cd,Zn)S nanocrystals depends on the Zn^2+\Cd^2+ ratio in the aqueous subphase. Their crystalline structures respond to the template mismatch both by twinning, as is the case for ZnS for which continuous compositional shift is observed, and by phase shift to hexagonal wurtzite, with pure CdS composition. The nanocrystals exhibited a continuous energy-gap shift, reflecting the Zn/Cd ratio in the solid solution.
RECONCILING CAPTURE-ZONE DISTRIBUTIONS AND GROWTH EXPONENTS: ROLE OF HOT PRECURSORS IN SUBMONOLAYER GROWTH OF HEXAPHENYL ON MICA
Theodore L. Einstein1, Josue R. Morales-Cifuentes1, Alberto Pimpinelli2
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Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to access the critical nucleus size \( i \) [1]. We summarize some extensive Monte Carlo simulations and especially experiments on several systems to which the GWD has been applied. In some cases, most notably parahexaphenyl (6P) on sputter-modified mica [2], the value \( i \) extracted from CZD differs from the [larger] values of \( i \) deduced from the growth exponent \( \alpha \) (island density \( N \) proportional to \( F^\alpha \) for flux \( F \)). Furthermore, while the scaling was good, the values of \( \alpha \) differed considerably at small and large \( F \), which was attributed to DLA (diffusion-limited aggregation) and ALA (attachment-limited aggregation) dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient ballistic adsorption (hot precursors), for the first time in a quantitative way from a rate-equation approach [3]. Two key parameters are the competing times of ballistic monomers decaying into thermalized monomers vs. being captured by an island. There are several other times and energies in the model. We obtain an implicit analytic solution and a convenient asymptotic approximation for limiting values of key dimensionless ratios. Our model exhibits non-monotonic crossover and several intermediate scaling regimes, marked by distinctive values of \( \alpha \) and an effective activation energy. One of these, rather than ALA, gives the best fit of the experimental data and a value of \( i \) consistent with the CZD analysis.

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stresses due to lattice parameter and thermal expansion coefficient mismatches between Si and Ge. Further optimization of the SEG process may be significantly assisted by atomistic simulation.

Methods: We begin by describing a validation process for a Tersoff-based model for the ternary Si-Ge-O system [1,2], in which we compare simulation predictions to detailed experimental data [3,4] for bulk SiO2 structural parameters, Si-SiO2 and Ge-SiO2 interface energies, and the Ge-on-SiO2 desorption energy. Using this validated interatomic potential, Ge deposition and islanding on an amorphous SiO2 surface was studied with direct molecular dynamics and the results compared to experimental measurements [4]. These quantitative comparisons were enabled by using an analytical rate model as a bridge between simulations and experiments, which are necessarily performed at deposition fluxes that are different by many orders of magnitude.

Results: The simulations are shown to provide accurate predictions of the island critical size and the scaling of island density as a function of temperature. We present some recent efforts at accelerating molecular dynamics simulations with "equation-free" coarse projective integration [5]. Here, coarse measures of the island size distribution dynamics are obtained from short molecular dynamics simulations and then used to evolve numerically the size distribution over large time intervals. In particular, we show that the reconstruction of atomic configurations from size distribution moments represents the key challenge in deposition simulations and we propose approaches for achieving this in a computationally tractable manner.

Conclusion and Outcome: We demonstrate that direct molecular dynamics simulation of atomic deposition may be employed, at least for some situations, at experimentally realistic conditions. Even so, emerging multiscale approaches will make such comparisons far more direct.


9:20 AM - 9:40 AM
KINETIC MONTE CARLO SIMULATIONS OF EPITAXIAL GROWTH OF WURTZITE GaN
Manjusha Chugh, Dr. Madhav Ranganathan
Indian Institute of Technology, Kanpur, Kanpur, India

GaN is a wide band gap material having many potential applications in Light Emitting Diodes (LEDs) and High Electron Mobility Transistors (HEMTs) and lasers. Our objective is to model MBE growth of GaN(0001) surface using lattice kinetic Monte Carlo (kMC) simulations and understand the effect of temperature and fluxes on the morphology of the growing crystal. Density functional theory based energy calculations are used to get the potential-energy surface (PES) and calculate the barriers for various processes involved in Homoepitaxial growth of GaN(0001). We used PWscf code of Quantum Espresso distribution for these calculations. These barriers for various processes are used as inputs in a lattice kMC simulation to model the crystal growth. On GaN(0001) surface, the diffusion barrier for N adatom is higher as compared to that of Ga adatom. Low diffusion barrier of N can be a reason for stacking faults in the grown crystals under Ga/N ratio < 1. We observed that as Ga/N ratio becomes greater than 1, N's diffusion barrier decreases. We identified a kind of rotation move for N atom in presence of another Ga atom in its vicinity. Thus, high quality crystals can be observed under slight Ga-rich conditions as also observed experimentally.

Starting from the understanding of atomic processes from first-principles calculations, we have developed a lattice kMC simulation for GaN(0001) growth. Slight Ga-rich conditions are needed to obtain good quality crystals. The effects of temperature and fluxes on the morphology of the surface are currently being studied.

9:40 AM - 10:00 AM
PREPARATION AND CHARACTERIZATION OF EPITAXIAL ERBIUM OXIDE FILMS
Wei Mao
The University of Tokyo, Tokyo, Japan

Single-phase nanocrystalline thin films of Er2O3 (440) has been first prepared using Si (001) substrates by ion beam sputter deposition at 700 oC at a pressure of < 10-7 torr and in-situ annealing at 750 oC at a pressure of < 10-9 torr. Er silicide formed during the deposition is eliminated via the annealing, which results in the single phase and the smooth surface of the Er2O3 thin films. Density functional theory calculations suggest that the spin polarized surface electronic density of states is absent when Er comes at the surfaces.
The primary limitation for greater implementation to this point has been the difficulty in growing single crystals of Lu₂O₃. The hydrothermal growth and study of bulk ZnSe single crystals offer a unique blend of physical, spectroscopic, and technological parameters that make them the gain media of choice for cost effective broadly tunable lasing in the Mid-IR [1]. The II-VI semiconductor hosts provide a low phonon cut-off, broad IR transparency, and high thermal conductivity. When doped with metal ions, these mid-IR gain media feature a four-level energy structure, an absence of excited state absorption, broad absorption bands overlapping with many convenient fiber laser sources, a broad vibronic emission band enabling wide tunability, and (for Cr doped II-VI media) high - close to 100% quantum efficiency of fluorescence at room temperature (RT). This combined with the low-cost mass production technology of crystal fabrication by post-growth thermal diffusion, as well as broad availability of convenient pump sources, make these materials ideal candidates for broadly tunable mid-IR lasing in CW, gain-switched, free running, and mode-locked regimes of operation. This talk summarizes fabrication challenges of post-growth thermal diffusion doped TM:II-VI gain media. The coefficient of diffusion could be increased by means of simultaneous gamma-irradiation during the thermal diffusion process [2]. The addition of γ-irradiation during the annealing process has demonstrated a significant increase in diffusion lengths of iron in ZnSe and ZnS, 25% and 50%, respectively. This technique shows promise for production of materials doped with a more uniform dopant concentrations, larger crystal size or increase concentrations of dopants such as large rare earth ions to levels which would otherwise be difficult to achieve with this technique. The talk also reviews a recent progress and practical applications of fiber-bulk mid-IR hybrid laser systems based on Er/Tm fiber-Cr and Fe doped II-VI wide band semiconductors providing access to the 1.9-6 μm spectral range with a high (up to 70%) efficiency, multi-Watt-level output powers, tunability in excess of 100nm, short-pulse (<30 fs) multi-watt oscillation, multi-Joule long-pulse output energy, and narrow spectral linewidth (<100 kHz).


High power tunable laser sources in the mid to longwave IR and THz are in a great demand due to the wide variety of military and commercial applications in security, industry, science, and medicine. Strong interest in this topic gradually led to exploring a number of nonlinear optical crystals that could access these wavelengths by frequency conversion in orientation patterned (OP) QPM materials. However, many of these materials have unavoidable shortcomings such as providing low output power, narrow range of transparency, poor tunability, low growth rate, high motor heating, broad absorption sources, high two-photon absorption or unavailability of high quality low cost wafers for preparation of OP-templates for a subsequent thick growth. This has necessitated continued research of new nonlinear materials, alternative growth approaches, and template fabrication techniques. ZnSe has a wide transparency range, which begins in the visible and continues into the IR beyond the absorption edge for ZnGeP₂, GaP and GaAs. Coupled with the high nonlinear susceptibility and low two-photon absorption (ZPA), ZnSe is a promising nonlinear QPM material.

Hydrothermal growth of bulk zinc selenide (ZnSe) single crystals using a platinum inner ampoule and CVD grown seeds has been explored. Crystals of high quality and purity were successfully grown using a combination of hydroxide and chloride mineralizers. Growth rates of the hydrothermally grown crystals were controlled by varying the temperature gradients. Solubility studies conducted reveal a solubility range of 1-3Wt% (weight percentage) at temperatures between 260 and 400°C. The higher crystallinity of the hydrothermally grown ZnSe crystals relative to the CVD grown seed was confirmed by HRXRD. The grown crystals were also characterized using FTIR and photoluminescence spectroscopy.

Lutetium oxide is a very promising host lattice for high power laser applications. It has a wide transparency window, exceptional chemical and thermal stability and good thermal conductivity. In addition the lutetium ion has almost the same ionic size and mass as most typical lasing ions (Yb, Er, Tm, Ho), so doping homogeneity should be good and the decrease in thermal stability upon doping is minimized. Previous work also demonstrated that the absorption and emission coefficient of Yb doped Lu₂O₃ is favorable for high power applications. The primary limitation for further implementation to this point has been the difficulty in growing single crystals of Lu₂O₃. The
material melts above 2450°C and is not soluble in convenient fluxes. This paper will describe progress made in the growth of single crystals of Lu2O3 as well as doped single crystals, using the hydrothermal method. Single crystals can be grown in concentrated hydroxide solutions at 600-650°C at 1-3kbar pressures. In addition such crystals can be readily doped with a variety of possible lasing ions. The detailed spectroscopy of a number of rare earth doped Lu2O3 single crystals will be reported, along with their emission spectra, and a preliminary evaluation as high power laser hosts will be discussed.

11:30 AM - 12:00 PM
THIN FILM GROWTH OF OPTICALLY ACTIVE CORRELATED OXIDES
Invited
Shriram Ramanathan
Harvard University, Cambridge, MA

I will present recent advances in synthesis of phase change materials like vanadium dioxide and rare earth nickelates and their electrical/optical properties. Of great interest are the ability of these materials to interact in a non-linear manner with radiation and sharp phase transitions under various external stimuli. The role of defects in influencing functional properties will be considered. Further, the ability to tune the optical and electrical properties by strain, substrate selection and deposition conditions will be examined. Finally, we will discuss non-thermal phase transitions that can be driven by electric fields and the recent discovery of new insulating phase that is accompanied by eight orders of magnitude resistance change at room temperature.
By including a strain-balanced superlattice in the GaAs middle cell, the efficiency of InGaP/GaAs/Ge multi-junction solar cells can be improved. Such a superlattice extends the absorption edge of the middle cell to 1.2 eV while avoiding lattice relaxation. The requirement of enough light absorption by InGaAs and efficient carrier extraction led us to the stepwise superlattice with GaAs layers in between InGaAs and GaAsP layers and the thickness was approximately 3 nm for each. 6°-off Ge substrates are commonly used for InGaP/GaAs/Ge cells for the purpose of eliminating twin dislocations in the GaAs layer on Ge. Therefore, the superlattice that we have developed should be grown on a 6°-off substrate in order for them to increase the current out of the GaAs middle cell. Step bunching on such a vicinal substrate induced layer undulation especially for InGaAs layers, making relaxation-free growth quite difficult. Low-temperature MOVPE was then attempted to suppress layer undulation, but increased carbon impurity level induced band bending and made carrier collection difficult. The use of triethyl-gallium (TEGa) instead of trimethyl-gallium (TMGa) dramatically improved the situation: carbon impurity remained at a sufficiently low level even at the low-temperature growth to suppress layer undulation. In addition, in situ monitoring of surface reflectance and reflectance anisotropy helped optimize the GaAsP barrier thickness to achieve efficient carrier collection from InGaAs absorber via tunneling and strain-balancing at the same time. Such findings and optimization allowed us to implement 100-period superlattice into the GaAs middle cell of the 3-junction cell grown on a 6°-off Ge substrate. Substantial improvement in current matching among subcells was achieved owing to the superlattice. Lastly and most importantly, a slight layer undulation helped carrier escape compared with a regular plane superlattice, meaning that “wire on well”-like superlattice will be the most promising structure for the application of high-efficiency solar cells.

11:00 AM - 11:20 AM
LATERAL PHASE SEPARATION IN COMMERCIALLY IMPORTANT (GA,AL)INP LAYERS GROWN BY MOCVD AND MBE
Andrew Norman¹, Kunal Mukherjee², Theresa Christian³, Nancy Haegel³, Angelo Mascarenhas¹, Eugene Fitzgerald², Pranob Misra³, Ting Liu¹, Arsen Sukiasyan³, Evan Pickett³, Homan Yuen¹
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GaInP and AlInP are of interest for a range of semiconductor devices including high efficiency multijunction solar cells, light emitting diodes, and transistors. For all these applications, optimum device performance requires an understanding of the nature, origin, and effect of composition modulations and atomic ordering that can occur during epitaxial growth. In this work we report a detailed study of lateral phase separation that can occur during the growth of AlInP and GaInP alloy layers by MOCVD and MBE. In both cases a lateral phase separation is found to occur preferentially along the [110] direction, Fig. 1. An in depth study of MOCVD AlInP by scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) revealed that the wavelength and amplitude of the composition modulation depended on the temperature used for growth. The composition modulation was found to evolve, from an initial small fluctuation, to reach a steady state after a finite thickness of layer growth that also depended on the growth temperature. The results are consistent with phase separation occurring via surface diffusion during growth. For the MBE grown GaInP layers, the lateral phase separation was found to result in anisotropic diffusion lengths, anisotropic mobility values, and strongly polarized photoluminescence (PL). For the MOCVD grown AlInP layers, the lateral phase separation was found to lead to a lowering of the PL peak energy, a broadening of the PL peak, and carrier trapping. These effects could have a significant impact on the performance of devices fabricated from these materials.


Figure 1. STEM HAADF image showing lateral phase separation in MOCVD AlInP layers grown at different temperatures. 202116.
GaAs, Bi/GaAs superlattice structures have promise for applications in longer-wavelength emission and solar energy harvesting. However, because Bi is essentially insoluble in GaAs, optimization of growth techniques to yield the high-quality epitaxial GaAs, Bi/GaAs superlattice structures with homogeneously distributed Bi within the GaAs, Bi layers that are needed for devices requires a thorough understanding of how Bi is incorporated in GaAs. To develop this understanding, this work probed the distribution of Bi atoms, in three dimensions and with near atomic spatial resolution, in OMVPE-grown GaAs, Bi/GaAs superlattice structures using atom probe tomography (APT). The GaAs, Bi/GaAs superlattice structures were grown on (001) GaAs substrates at 390°C. The Ga and Bi reactants were introduced into the reactor in asynchronous short pulses during growth of the Bi-containing layers. The sharp needle-shaped specimens for APT were prepared by focused ion beam methods including in-situ lift-out and annular milling steps. The APT experiments were conducted in a Cameca 3000X Si local electrode atom probe (LEAP) with laser pulsing. The APT reconstruction and analysis were done in IVAS™ 3.6.6 software.

A 1D Bi concentration profiles along the growth direction deduced from the image intensity of high-resolution Z-contrast TEM images revealed the concentration profiles that deviated substantially from the square wave shape the growth sequence was intended to produce. This Bi distribution in the growth direction was unexpected, but also reproduced in each period of the superlattice structures. The 3D pulsed-laser APT results corroborated these profiles. More importantly, they complemented the TEM
investigations by providing the lateral distribution of Bi normal to the growth direction at near atomic spatial resolution. Nearest
neighbor distribution analysis of Bi deduced from the APT indicated a statistically random lateral distribution of Bi, without clustering,
which suggests that Bi is distributed rather homogeneously within planes parallel to the substrate even when the concentration
profile in the growth direction is complex. In conclusion, APT offered 3D Bi mapping with near atomic spatial resolution for the
GaAs$_{1-x}$Bi$_x$/GaAs superlattice structures. Here APT indicated that Bi is homogeneously distributed within the growth planes of
OMVPE-grown superlattice structures even in the absence of sharp square wave shaped Bi concentration profile along the growth
direction.

Figure. 3D Bi atom distribution in GaAs$_{1-x}$Bi$_x$/GaAs superlattice structures using APT.

11:40 AM - 12:00 PM
STRAIN-MEDIATED INTERFACIAL DIFFUSION AND SHIFTS IN INTERSUBBAND TRANSITION ENERGIES IN ALN/ALGAN SUPERLATTICES
Michael W. Moseley, Andrew A. Allerman, Inès Montaño, Jonathan J. Wierer, Jr., Anna Tauke-Pedretti, Erik Skogen, G. Allen Vawter
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The large conduction band offset in AlN/GaN heterostructures (1.75–2 eV) enables intersubband transitions (ISBTs) within the
telecommunications spectrum (1.3-1.55 μm). Ultra-fast electron relaxation times (150-300 fs), minimal thermal sensitivity to
transition energy, and high saturable optical power are desirable for electro-absorptive optical modulation. However, telecom-
relevant ISBTs in AlN/GaN heterostructures necessitates smooth, abrupt interfaces with well widths smaller than 2 nm. Tensile
strain in AlN barrier layers has been suggested to broaden AlN/GaN heterostructure interfaces, resulting in a red-shift of the ISBT
optical absorption. In this study, the effect of epilayer strain on absorption spectra in III-nitride ISB superlattices (SLs) grown by
MOCVD is explored.
Three pseudosubstrates were prepared with different in-plane lattice constants: 3.1091 Å (AlN on sapphire), 3.1132 Å (Al$_{0.65}$Ga$_{0.35}$N on
AlN on sapphire), and 3.1293 Å (Al$_{0.65}$Ga$_{0.35}$N on sapphire). Coupled quantum well 10-period AlGaN/AlN ISB modulator structures
were regrown concurrently on all three pseudosubstrates. The targeted thicknesses and compositions of 14 Å Si$_{0.03}$Al$_{0.07}$Ga$_{0.93}$N / 15 Å
AlN / 26 Å Si$_{0.15}$Al$_{0.15}$Ga$_{0.7}$N / 34 Å AlN were based on band diagram simulations. Both the narrow and wide AlGaN wells were silicon
doped ($N_0 \sim 4 \times 10^{19}$ cm$^{-3}$) to observe the optical absorption (~1.5 μm and 2.2 μm respectively) in each well.
Optical absorption at 1.53 μm was achieved in the ISB structures grown on AlN. However, the peak absorption wavelength of the
ISB SL structures grown on AlGaN were red-shifted up to 1.62 μm and trended with increasing average in-plane lattice constant.
Transmission electron microscopy measurements revealed that the layers in the ISB SL with the smallest average in-plane lattice
constant remained abrupt and uniform. However, blurring of the interface and undulations in well thickness were observed in the SL
structure with the largest average in-plane lattice constant and consequently the most tensile strain in the AlN barriers.
Band diagram simulations were performed to observe the theoretical effect of compositionally graded heterointerfaces around the
wells, and the red shift in simulated peak absorption spectra was reproduced. Therefore, it was determined that the strain state of
the underlying epilayer template has a significant effect on the performance of the subsequently grown ISB structure. This work
illustrates the necessity to minimize tensile strain in barrier layers of III-nitride based ISB superlattices to achieve optical absorption
at telecom wavelengths.
Figure 1. Optical absorption spectra of the ISB modulator structures grown on sapphire concurrently on (a) AlN on sapphire (3.1091 Å) and (b) Al$_{0.61}$Ga$_{0.39}$N on sapphire (3.1293 Å). The lowest energy peak corresponds to the 26Å reservoir well, while the highest energy peak corresponds to the 14Å absorbing well in the coupled-QW structure. Shown in (c.) and (d.) are high magnification cross sectional TEM of the ISB modulator structures grown on pseudosubstrates with the (c) smallest and (d) largest average in-plane lattice constants. Note the interfacial blurring in (d.).
New soft magnetic materials will be vital for the next generation of power conversion electronics necessary to efficiently bring new renewable energy sources online. Magnetic nitrides, specifically gamma'-Fe3N, if manufactured in bulk form, could offer a new class of affordable and better performing soft magnetic materials. According to experimental results from thin films and/or theoretical calculations many of the magnetic nitrides would have magnetic moments well in excess of current state of the art soft magnetic materials and even bulk iron. Furthermore, the experimental data and theoretical predictions that do exist suggest these materials would be both magnetically soft and more electrically resistive than other soft magnetic alloys. Therefore, magnetic nitrides would be ideally suited for use in applications such as transformer cores. Some of the magnetic nitrides have been fabricated as thin films or inclusions in other materials while magnetic properties of other nitride materials have only been predicted. In collaboration with UC Davis, Sandia National Labs has developed new routes (patent pending) to synthesize iron nitride powders via a either a two-step ball milling process or the electrochemical solution growth (ESG) technique. The iron nitride powders are then consolidated using a low temperature field assisted sintering technique (FAST). FAST enables the direct consolidation and shaping of crystalline gamma'-Fe,N transformer and inductor cores from raw starting materials in a matter of minutes, without the decomposition of iron nitrides that would occur using conventional sintering techniques. Experimental results including the synthesis of iron nitrides, their consolidation, and magnetic characterization will be presented.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:50 AM - 11:10 AM
SYNTHESIS AND CHARACTERIZATION OF SILICON DICHALCOGENIDES, SI(SEXS1-x)2, FOR PHOTOVOLTAIC APPLICATIONS

Chen Chen1, XiaoTian Zhang1, Lakshmi Krishna1, Chito Kendrick1, ShunLi Shang1, Eric Toberer1, Zhi-Kui Liu1, Reuben Collins2, Adele Tamboli2, Joan M. Redwing*1
1Department of Materials Science and Engineering, Materials Research Institute, Pennsylvania State University, University Park, PA, 2Department of Physics, Colorado School of Mines, Golden, Colorado, CO, National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, Colorado, CO

Silicon dichalcogenides alloys of selenium and sulfur, Si(SexS1-x)2, have bandgap energies in the range of 1.6-3.0 eV, which is very interesting for a broad range of optoelectronics with the lower end ideal for the top cell of a tandem photovoltaic device based on a monocristalline silicon bottom cell [1]. Initial studies of these materials were carried out in the 1980s, mainly focusing on the synthesis and structural characterization of the binary compounds of SiSe2 and SiS2 [2]. The crystalline form of SiSe2, for example, consists of long edge-sharing chains of SiSe4 tetrahedra, which are held together via van der Waals forces. In the glassy or amorphous phase, the chains become disordered with cross-linked corner-sharing tetrahedra. There is limited information on the optical properties and chemical stability of these materials and their ternary alloys. In this study, a series of Si(Se-xS1-x)2 bulk crystals were synthesized via congruent melting by varying the stoichiometric ratios of the starting materials. Stoichiometric amounts of high purity Si, Se and S powders were introduced into one end of a quartz tube which was then evacuated and sealed under vacuum. The powders were annealed at 1100°C for 8 hours and then cooled to room temperature. Raman measurements were used for phase identification to confirm the formation of SiSe2, SiS2 and Si(SexS1-x)2 (x = 0.25, 0.5, 0.75) alloys, validating the presently predicted phase stability from first-principles calculations. The sample color was observed to vary from white for SiS2 to orange for Si(Se,S) to dark red for SiSe2. The UV/visible/IR transmission measurements showed an increase in absorption in the range of 1.6-1.9 eV for SiSe2 and 2.4-3.0 eV for SiS2, indicating that the optical band gap varies from 1.6 eV to 3.0 eV in the ternary alloys of Si(SexS1-x)2, and also agreeing with the present first-principles predictions. The reactivity of SiSe2 and SiS2 with H2O vapor in the air which leads to oxidation and H2Se or H2S evolution from the surface complicates characterization and device fabrication. Effort to passivate or encapsulate the surface to prevent oxidation will be discussed.

Reference

Cu2ZnSnS4 is a new material with low extraction cost. It belongs to Cu-Zn-Sn quaternary system and has recently attracted great attention as promising photovoltaic material. Due to its interesting properties such as a band-gap of 1.5 eV and a large absorption coefficient in the order of 10^4 cm^{-1}, this material is considered as ideal for effective phonon absorption and photo-generation. Since the sulfur is an important element in the stoichiometric and the performance of Cu2ZnSnS4 phase, its content effect on the purity, stability and crystallization of Cu2ZnSnS4 material has been investigated. It was found that, for an excess sulfur starting concentration from 3wt% to 12wt%, high purity Cu2ZnSnS4 single phase compound could be obtained. In this sulfur range composition, Cu2ZnSnS4 alloy has been synthesized and vertically well textured along the melt flow. Depending on the sulfur concentration in the starting charge, it is possible to control the solidification and the morphology of Cu2ZnSnS4 phase. Moreover, following this result, it is possible to control the solidification process and to grow crystal under stationary stable regime.

The present work was undertaken with the purpose of studying the effect of the sulfur on the kinetic formation of Cu2ZnSnS4. The influence of sulfur on the purity and the single phase domain of Cu2ZnSnS4 compound was investigated. According to its phase diagram, single phase Cu2ZnSnS4 material can be formed only in a very narrow region. As a result, parasite binary and ternary stable phases such Cu2S and Cu2SnS3 can act as a barrier for the Cu2ZnSnS4 formation. On the other hand, to deal with the volatility of sulfur, we proceeded to excesses of sulfur to avoid the loss of the latter.

It was found that, for an excess sulfur starting concentration from 3wt% to 20wt%, high purity Cu2ZnSnS4 single phase compound could be obtained. In this sulfur range composition, Cu2ZnSnS4 alloy has been synthesized and vertically well textured along melt flow. Depending on the sulfur starting composition, binary SnS and ternary Cu4Sn7S16 phases with small amounts can be precipitated and their concentration is connected to the initial sulfur quantity in the starting charge. We found that the prepared samples with different sulfur excesses include a similar main phase and we obtained quasi single phase compounds.
THE DETERMINATION OF PBSNTE NANOLAYERS CRITICAL THICKNESS PREPARED BY MBE TECHNIQUE ON BAF2 (111) SUBSTRATES

Alexander M. Samoylov¹, Anton S. Toreev¹, Alexander E. Klimov², Alexey Akimov², Vladimir N. Shumsky²

¹Voronezh State University, Voronezh, Russian Federation, ²Russian Academy of Science, Institute of Physics of Semiconductors, Novosibirsk, Russian Federation

At fabrication of a wide range of optoelectronic devices operating in IR band of spectrum lead chalcogenides and their solid solutions are the worthy collaterals of InSb and Cd1-xHgxTe alloys. According to preliminary calculations, in Pb1-xSnxTe and PbTe nanoscale films the transition from classic type size effects to size quantum effects would be watched within a thicknesses interval from 25 nm up to 150 nm [1].

The main purpose of the present work is to verify the possibility of size quantum effects in Pb1-xSnxTe/BaF2 (111) nanoscale heterostructures. For this purpose the evolution of electrical parameters of Pb1-xSnxTe films (x = 0.26) on BaF2 (111) substrates has been studied depending upon their thickness and preparation procedure.

In this work Pb1-xSnxTe/BaF2 (111) epitaxial heterostructures were fabricated by MBE technique. MBE apparatus is equipped with electrons diffraction (ED) adjustment, quartz balance for growing layer's mass measurements, and thermocouple manipulator mechanism for the control of substrate surface temperature. The measurements of conductivity and Hall coefficient were carried out by four-probe Van der Pauw technique within temperature interval 4.2 - 300 K. The experimental results were compared to the values of the same parameters of Pb1-xSnxTe/BaF2 (111) heterostructures with chalcogenides layer thickness d more than 1,000 nm.

In this work Pb1-xSnxTe/BaF2 (111) nanoscale heterostructures intended for electrical parameters measurements were prepared by two different procedures. First of them was the direct films deposition from the source with ground Pb1-xSnxTe single crystal and annealing at T = 680 K during two hours. The processes of Pb1-xSnxTe films deposition and annealing have been carried out under ED control of their real microstructure. The second procedure was thinning of previously formed Pb1-xSnxTe films with d > 1,000 nm up to nanoscale size by polishing in etching solution.

It has been shown that for Pb1-xSnxTe films with d 1,000 nm. In addition, at approximately the same thickness Pb1-xSnxTe films prepared by first technique are characterized by charge carrier mobility values, which were in 3 - 8 times less than the values for layers fabricated by second technique. It has been assumed that the electrical parameters degradation with decrease in thickness of nanoscale films is caused by enhancement of the role of defect interface Pb1-xSnxTe/BaF2 layers during charge carrier transport processes.

References
A highly competitive Continuous Czochralski (CCz) method of crystal pulling has been developed at SunEdison, is under continuing optimization, and is being expanded into high volume manufacturing to produce large amounts of high quality silicon for photovoltaic conversion applications. The method is particularly advantageous in production of crystals with dopants exhibiting segregation coefficients substantially different from unity, including phosphorous for n-type silicon and a variety of small segregation coefficient p-type dopants. The method can economically be used to produce crystals with either low or high resistivity values. There are several benefits of the CCz approach for single crystal silicon with segregation coefficients substantially different from unity. Melted dopant and polysilicon introduction during crystal growth allows for more uniform axial resistivity than batch Cz, resulting in improved crystal manufacturing yield. The larger crystals grown by CCz can be decoupled from crucible size and crystal diameter. The crystal length is determined by “height of building” (length of pull chamber) instead of crucible size. This allows longer crystals to be made in a run without increasing the size and cost of the consumables or the production equipment. The continuous supply of polysilicon during body growth allows shortening of the sequential charge-melt-stabilize-grow-remove cycle for crystals. CCz provides quasi-steady state heat and mass transfer conditions during pulling by continuously adding poly-silicon and electronic impurities (“dopant”) during the crystal growth itself. Macroscopic crystal axial impurity variation is inherent in the Cz “batch” growth process due to macro-segregation phenomena during normal freezing conditions. By continuously controlling charging of both poly-silicon and dopant via CCz, the resistivity dictated by dopant macro-segregation can be directly controlled, and produces repeatable resistivity mono wafers. The conditions for constitutional supercooling can be managed effectively for crystal resistivity control in the CCz approach for single crystal silicon with segregation coefficients substantially different from unity, including phosphorous for n-type silicon and a variety of small segregation coefficient p-type dopants. The method can economically be used to produce crystals with either low or high resistivity values.
The photovoltaic (PV) industry is in a phase of rapid growth, annually increasing by 44% for PV installations from 2000 to 2013. To further develop PV market, further cost reduction and efficiency improvement are required, and technology innovations become significant, especially in low-cost silicon growth. At present, 55% of the silicon wafers are cut from multicrystalline silicon. Multicrystalline silicon is less expensive, but exhibits lower conversion efficiency than monocrystalline silicon. Thus, further improving the efficiency of multicrystalline silicon has recently become a main concern in research and industry communities. BP Solar first proposed a multiseed casting technique for growing multicrystalline silicon with a monocrystalline-like (mono-like) structure with fewer defects than conventional multicrystalline silicon. Using this technique, BP Solar produced square wafers of 156 mm in length and 130 μm in thickness, which exhibited a high conversion efficiency of 18%. However, this technique encountered many challenges. A main challenge is that dislocations are formed between seeds at the beginning of growth and then propagate along the grain boundaries with explosive multiplication. The explosive multiplication of dislocations may break down the crystallization process and dramatically reduce the conversion efficiency of silicon. Therefore, to make the multiseed casting technique acceptable in industry, it is necessary to first reduce dislocation density.

To overcome dislocation generation and propagation with explosive multiplication in the multiseed casting method, we proposed a new one-seed casting technique, in which only one seed was placed at the bottom of the crucible and an entire monocrystalline ingot is grown from that seed. The advantage of our method is that the grown ingot is a fully single crystal with no grain boundaries, and thus the explosive multiplication of dislocations along grain boundaries does not occur anymore. Therefore, this technique can help us grow high-quality and large-size monocrystalline silicon with a cost similar to that of multicrystalline silicon.

To realize this technique, two challenges—polycrystalline nucleation on crucible wall and dislocation multiplication inside crystal—needed to be addressed. Numerical analysis was used to develop solutions for these challenges. Based on an optimized furnace structure and operating conditions from numerical analysis, experimental were performed to grow monocrystalline silicon using one-seed casting technique. The results revealed that this technique is highly superior to popular high-performance multicrystalline technique and multiseed casting mono-like technique.

Acknowledgements
This work was partly supported by the New Energy and Industrial Technology Development Organization under the Ministry of Economy, Trade and Industry (METI), Japan.
TWIN GENERATION DURING CZOCHRALSKI-GROWN OF SI AND SIDGE
Ichiro Yonenaga, Kaisei Inoue, Kentaro Kutsukake, Yutaka Ohno
Tohoku University, Sendai, Japan

In Czochralski-growth of Si crystals, dislocations generated during a seeding process can be almost perfectly eliminated by the Dash-necking with a 3-4 mm neck. However, it is known that several dislocations and twins generate during the shoulder part growth stage, increasing the diameter, after the necking of Si, especially heavily doped with impurity. Here, we report twin formation in Si crystals heavily doped with impurities (Ga, In, P, B) and SiGe alloy crystals and discuss the plausible mechanism.

Si crystals doped with impurities and SiGe crystals with various compositions, both about 1 inch in diameter, were grown by the Czochralski technique. Defects and growth striation in the top portion of grown crystals were observed by X-ray topography and an optical microscopy. Twins generated from the periphery in Si heavily doped with P, As, and Ga, but did not in B-doped Si. In these Si the stacking fault energy slightly varied. Twins were observed in SiGe alloys of Si-rich and with intermediate Si content, where the stacking fault energy of SiGe alloy is 55-61 mJ/m², intermediate between those of Si and Ge. In literatures, twin formation is supposed to be closely related to the formation of growth facets. From the present studies, it is also known that twin generation in heavily impurity-doped Si and SiGe alloys is controlled by two factors: high strain/stress originating from the axial and radial composition or temperature variations and stacking fault energy.

9:30 AM - 9:45 AM
LATTICE PARAMETER OF IV-IMPURITY DOPED SI: REVISITED TO VEGARD’S LAW
Ichiro Yonenaga, Raira Gotoh, Kazuhiko Omote, Toshinori Taishi, Yuki Tokumoto, Kentaro Kutsukake, Yutaka Ohno
Tohoku University, Sendai, Japan, RIGAKU Corporation, Akishima, Japan, Shinshu University, Nagano, Japan, University of Tokyo, Tokyo, Japan

Impurity doping into semiconductors is conducted with a purpose to control the electrical properties for device applications. In Si, recently, the doping is practically significant to coordinate the lattice parameter for applying the crystals as an epitaxial substrate of lattice-matched with or small misfit against a desired foreign film. Such so-called strain or lattice parameter engineering can be performed effectively under a permission of the accurate knowledge on the lattice parameter of material in terms of the impurity concentration. It is generally recognized that the lattice parameter of impurity-doped materials changes with impurity concentration following Vegard’s law macroscopically, leaving microscopic aspect on local atomic structure around a doped atom. Thus, we report an accurate study of the change in a lattice parameter when single-crystal Si is substitutionally doped with neutral IV group impurities in a concentration of 4 × 10¹⁵ cm⁻³ in maximum.

The lattice parameters of Si crystals heavily doped with Sn and Ge grown by the Czochralski method were measured by an accurate X-ray method at RT. The lattice parameter of a high-purity FZ-Si was referred as a standard of the lattice parameter of Si. Impurity concentrations were determined by WDX measurement. The lattice parameter depends linearly on the concentration of Sn and Ge impurities in the crystals macroscopically with a lattice expansion/contraction coefficient, the slope of the linear dependence, 3.8 × 10⁻⁵ and 8.3 × 10⁻⁵ cm⁻³, respectively. The lattice expansion/contraction parameter was given by the misfit strain of the impurity atom. However, the followings are noteworthy: Some contraction from the Vegard’s behavior observed in Sn-doped Si may originate in a number of grown-in point defects as vacancy. SiGe alloys, as a heavily doped case, are known to follow the Vegard’s behavior on the lattice parameter macroscopically, while macroscopically the bond length and angles both change with the composition, i.e., SiGe is imperfect Pauling-type. In the paper, effects of other impurities on the lattice parameter of Si will be included for discussion of the microscopic aspect of atomic structure.

9:45 AM - 10:15 AM
SCALE UP OF DS-AND CZ-SILICON GROWTH PROCESSES UNDER TMF
Invited
Natasha Dropta, Frank M. Kiessling
Leibniz Institute for Crystal Growth, Berlin, Germany

The differences between the Cz and DS processes are significant in terms of a growth equipment, growth conditions and crystal properties, e.g.: i) crucibles are either cylindrical with a hemispherical bottom (Cz) or rectangular (DS), ii) crucibles are either predominantly heated from the side (Cz) or from the top and bottom (DS) leading to inverse axial temperature gradients and consequently to a different intensity of the buoyancy forces, iii) crucibles are rotating (Cz) or are stagnant (DS) that may cause a competition between the natural convection and the Coriolis’ forces, iv) convection has to be either dampened (Cz) or favorably enhanced (DS) etc. In spite of these differences, both processes share a common approach to improve the economy: to reach higher crystallization yields with up scaled crystal sizes while preserving the material quality. So far scaling up of DS-Si crystals to G7 size and Cz-Si crystals to 450mm in diameter was demonstrated [1,2], but due to insufficient crystals quality, these processes still haven’t reached the industrial maturity.

The control of growth conditions at the S/I interface is crucial for the growth of high quality crystals. For that purpose, travelling magnetic fields (TMFs) generated by KRISTMAG® heater magnet module (HMM) were successfully applied [3]. Despite many research studies at the lab scale, transfer of technology between different scales is still empirical and limited to low scale up ratios.

The aim of this paper is: (i) to derive a set of similarity principles for modeling of DS-Si and Cz-Si processes in TMF so that a numerical model can exactly reproduce the coupled transport phenomena and (ii) to verify the obtained numerical results with experimental data that are on disposal. Particularly, we studied mc-Si DS growth in real G1, G2 and G5 setups [4] (Fig.1) and we simulated Cz-Si growth in 23in. and 6in. crucibles, always considering furnaces provided with KRISTMAG® HMMs.

References
idle time has costs of power, argon, manpower and quartz plus hotzone wear. Either after initia
For any Manufacturing operation, time is costly. In particular for Cz or CCz crystal growth of solar monocrystal product in
Small changes in temperature in high temperature furnace systems like crystal growth can be modeled as a first
This paper discusses newer, high volume applications which require low-cost, high performance sapphire and how this market can
be addressed by growing world’s largest sapphire boules of 500mm diameter, 300kg using controlled heat extraction system
(SCHES). Sapphire has excellent mechanical and optical properties. It has been used for high strength, abrasion, sand erosion and corrosion resistant applications. With a melting point of 2040°C it is stable at high temperatures. In addition, it has good optical properties - high transmission in the vacuum ultra-violet through near infra-red wavelength range. However, it has been considered a specialty material and used for custom designed parts. Such applications do not require large volumes. Use of sapphire for large volume markets requires lower production costs. Production of blue LEDs is one such high-volume application where sapphire has been used as a substrate in recent years. This application requires c-plane substrates. Traditional techniques in the sapphire industry use a-plane orientation to grow sapphire crystals, which results in very poor material utilization and higher costs. Cover glass for wearable devices and screens for smart phones and other such devices is a more recent and a much higher volume application for sapphire.
The SCHES approach developed c-plane growth of large sapphire boules specifically for LED applications. With c-orientation over 75% material utilization is achieved compared to 35% limited from a-plane grown crystals using conventional technology. A recent emphasis has been on growing very large sapphire boules to reduce costs even further. Along with a heat zone which is low cost, long lasting and reproducible, a reusable crucible also gives further cost reductions. All these features have been combined with full automation so large scale production can be set up at a high ramp rate.

SYNCHROTRON TOPOGRAPHY STUDIES OF THE ORIGINS AND EVOLUTION OF DEFECTS IN INDUSTRIALLY GROWN 4H-SIC SUBSTRATES AND EPILAYERS
Invited
Michael Dudley
Stony Brook University, Stony Brook, NY
A review will be presented of recent monochromatic and white beam synchrotron topography based studies of Physical Vapor Transport (PVT) grown 4H-SiC substrate boules and Chemical Vapor Deposition (CVD) grown 4H-SiC homo-epitaxial layers. The methodologies used in applying these techniques to determine the origins and evolution of the various defect structures in the boules and epitaxial layers will be elucidated. In particular, criteria used in distinguishing grown-in from deformation induced defects will be discussed. Contrast observed from the various dislocations present in the crystals will be explained, and it will be shown how contrast simulation can be used to identify the detailed characteristics of the dislocations (for example, both Burgers vector sign and magnitude). Application of the various techniques to the complete analysis of the distribution, character and origins of grown-in c-axis screw dislocations, deformation induced basal plane dislocations (BPDs), and grown-in threading edge dislocations in PVT-grown substrates will be discussed. Formation of stacking faults will also be discussed. In addition, dislocation behavior during homo-epitaxy on offset substrates will be presented. Studies carried out before and after epilayer growth have provided insight into the initial origins of the observed relaxation processes involving the creation of interfacial dislocations (IDs) and half loop arrays (HLAs). These processes are initially driven by thermal stress resulting from radial temperature gradients experienced by the wafer whilst in the epi-chamber. These processes provide screw oriented segments that pierce the advancing epilayer surface that initially replicate as the crystal grows. Once critical thickness is reached these screw segments glide sideways under mismatch induced stress leaving IDs and HLAs in their wake. The origin of the mismatch stress is shown to be associated with doping induced lattice parameter differences at the growth temperature.

RAPID FURNACE THERMAL STABILIZATION
Steve Kimbel
SunEdison Inc, St. Peters, MO
Small changes in temperature in high temperature furnace systems like crystal growth can be modeled as a first-order with delay response to a power input change. After the delay there is an exponential change in temperature from one steady-state temperature value to the next. We can achieve faster response by overdriving, or “gapping” the power. A resonant gap consists of an overdrive of the desired power change \( P \), by a factor \( k \), followed after \( t_{PW} \), by a decrease to the desired power change, \( P \). A derivation of \( t_{PW} \) will be provided during the talk, but the effect on temperature response of a tuned power gap is shown below, and the response effect is clear.
For any Manufacturing operation, time is costly. In particular for Cz or CCz crystal growth of solar monocrystal product in-process idle time has costs of power, argon, manpower and quartz plus hotzone wear. Either after initial meltdown or between ingots, we
would like to quickly stabilize the furnace at the target temperature. Taking the simple approach of turning on a temperature control loop after a major disturbance like a refill can generate very large temperature fluctuations. Unlike the model above, a starting stable temperature from which to compute a power change normally does not exist, however desired temperature and approximate final power are normally known. With these and process response dynamics, one can generate a real-time regressive prediction of when an overdriven power should be returned to the final power value to quickly approach the target temperature, thus minimizing, with some further closed-loop control, the settling time. The steps are:
1. Based on the starting temperature error, pick a value of power overdrive, and set it as soon as practical.
2. Regressively fit the stream of temperature data to the process characteristic response, and compute an ultimate temperature.
3. Decrease the power to the approximate final power when a projection of the future temperature reaches the desired temperature.
4. Turn on temperature fine control loop. The computations to generate the regressive fit in step #2 will also be reviewed in the talk.

### Equipment and Methods for Growing Large Diameter 4H SiC Boules for Power Applications

**Eugene Tupitsyn, Neel Dhanaraj, Jeffery Wyatt, Stan Hemstad, Govindhan Dhanaraj, Larry Rowland**
Aymont Technology Inc., Ballston Spa, NY

Silicon carbide (SiC) is a semiconductor material which is replacing and outperforming the conventionally used silicon crystal in power applications. The wide bandgap of SiC results in a low leakage current even at high temperatures. SiC single crystals are also becoming popular as Moissanite gem stones competing with diamond because of their excellent brilliance and other properties. However, at present, the production of large size and high quality SiC single crystals is limited to a few industrial entities worldwide. The seeded physical vapor transport (PVT), commonly known as the modified Lely method, which exploits the sublimation at above 1800°C is the only proven method for the industrial production of SiC boules. However, fabrication of the PVT system for the growth of SiC is highly instrumentation oriented, and also due to its commercial importance, the know-how, and technical details are scarcely available in the literature. PVT SiC growth systems with the process technology are not easily available commercially, and the SiC growth industries develop these systems in-house and optimize the growth conditions. The complexity is due to the fact that the operating temperatures are extreme (2100-2500°C) and monitoring and controls are difficult. The growth process occurs in an nearly air-tight graphite crucible and it is not feasible to observe the growing boule or determine experimentally the exact thermal conditions in the growth zone due to high operating temperatures and the opacity of the graphite crucible. Seed mounting technologies are still kept as industry secret. It is difficult to control the radial gradients when the diameter reaches close to 6 inches or beyond. With full modeling knowledge as well as outstanding expertise in equipment and the process technology, Aymont has developed precisely controllable SiC growth systems and process for growing large boule with independently controllable axial as well as radial gradients. The technical details on the design and fabrication of the SiC PVT system, hot zone, modeling, crystal growth and characterization results are presented.

### Analysis of the Effect of Symmetric and Asymmetric Cusp Magnetic Fields on Solidification Interface During Czochralski Silicon Growth

**Parthiv Daggolu**, ALEX GALYUKOV*, Alexey Kondratyev*
1SunEdison Semiconductor LLC, St Peters, MO, 2STR US Inc, Richmond, VA

With the use of 300 mm silicon wafers for industrial semiconductor device manufacturing, the Czochralski (Cz) crystal growth process has to be optimized to achieve higher quality and productivity. Numerical studies based on 2D global thermal model combined with 3D simulation of melt convection are widely used today to save time and money in process development. Melt convection in large scale Cz Si growth is controlled by a cusp or transversal magnetic field (MF) to suppress melt turbulence. MF can be optimized to meet necessary characteristics of growing crystal, in terms of point defects, as MF affects melt/crystal interface geometry and allows adjustment of the pulling rate. Among the different knobs associated with Cusp magnetic field, the nature of its configuration, going from symmetric to asymmetric, is also reported to be an important tool for the control of crystallization front. Using 3D unsteady model of CGSim software, we have studied these effects and compared with several experimental results. In addition, physical mechanisms behind these observations are explored through a detailed modeling analysis of the effect of asymmetric cusp MF on convection features governing heat transport in Si melt.

### Effects of the Power Arrangement and Hot Zone Design During the Growth of Large Size Multicrystalline

9:45 AM - 10:00 AM

**Eugene Tupitsyn, Neel Dhanaraj, Jeffery Wyatt, Stan Hemstad, Govindhan Dhanaraj, Larry Rowland**
Aymont Technology Inc., Ballston Spa, NY

9:45 AM - 10:00 AM

**Equipment and Methods for Growing Large Diameter 4H SiC Boules for Power Applications**

**Eugene Tupitsyn, Neel Dhanaraj, Jeffery Wyatt, Stan Hemstad, Govindhan Dhanaraj, Larry Rowland**
Aymont Technology Inc., Ballston Spa, NY

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**Analysis of the Effect of Symmetric and Asymmetric Cusp Magnetic Fields on Solidification Interface During Czochralski Silicon Growth**

**Parthiv Daggolu**, ALEX GALYUKOV*, Alexey Kondratyev*
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With the use of 300 mm silicon wafers for industrial semiconductor device manufacturing, the Czochralski (Cz) crystal growth process has to be optimized to achieve higher quality and productivity. Numerical studies based on 2D global thermal model combined with 3D simulation of melt convection are widely used today to save time and money in process development. Melt convection in large scale Cz Si growth is controlled by a cusp or transversal magnetic field (MF) to suppress melt turbulence. MF can be optimized to meet necessary characteristics of growing crystal, in terms of point defects, as MF affects melt/crystal interface geometry and allows adjustment of the pulling rate. Among the different knobs associated with Cusp magnetic field, the nature of its configuration, going from symmetric to asymmetric, is also reported to be an important tool for the control of crystallization front. Using 3D unsteady model of CGSim software, we have studied these effects and compared with several experimental results. In addition, physical mechanisms behind these observations are explored through a detailed modeling analysis of the effect of asymmetric cusp MF on convection features governing heat transport in Si melt.
SILICON INGOTS BY THE SEEDED DIRECTIONAL SOLIDIFICATION PROCESS

Szu-Han Liao, Jyh-Chen Chen, Chun-Hung Chen, Yen-How Huang, Cheng-Jui Yang, Huang-Wei Lin

1 National Central University, Taoyuan, Taiwan, 2 Sino-American Silicon Products Inc, Hsinchu, Taiwan, 3 Sino-American Silicon Products Inc., Hsinchu, Taiwan

In this study, numerical simulation has been carried out to investigate the thermal field and the flow field in the furnace during the growth of 800 kg multicrystalline silicon ingot by the seeded directional solidification process. The heat transport during the growth is strongly affected by the heat extraction from the crucible support and the insulation condition of cage. The flatter crystal-melt interface shape can be get by changing the position of crucible support as well as adding the insulation block at the insulation cage. The side heater position is also one of the important factors affecting the temperature distribution and the crystal-melt interface shape.
Thursday, August 6, 2015
8:00 AM - 10:00 AM

Biological, Biomimetic, and Organic Crystallization (ACCGE) 1

Location: Amphitheater
Session Chair(s): Sidney Omelon & Roland Kroeger

8:00 AM - 8:30 AM
MINERAL NUCLEATION AND GROWTH ON FUNCTIONALIZED SURFACES
Maria Sushko¹, Donghai Me¹, Robert Darkins², Dorothy Duffy², Jun Liu¹
¹Pacific Northwest National Laboratory, Richland, WA. ²University College London, London, United Kingdom

Controlling the growth of inorganic materials on organic templates poses many challenges, but also opens vast opportunities for materials design. One of the important and yet unresolved questions is how does mineral growth affect the template structure. We present the theoretical study of titania nanoparticle nucleation and growth on functionalized graphene surfaces and on surfactant templates supported on graphene surface. We show that graphene functionalization, which modifies its interfacial chemistry, determines polymorph selection for nucleating titania nanoclusters. During the growth process on surfactant templates titania nanocrystals are initially confined between surfactant hemicylindrical micelles until they reach a critical size. Subsequent growth leads to at first partial and then complete rearrangement of the template structure to a monolayer configuration, which changes the mechanism of nanoparticle growth from predominantly thermodynamic to predominantly kinetic. The critical nanoparticle size can be controlled by controlling the stability of surfactant template with symmetric and asymmetric electrolytes. Using an example of surfactant-directed growth of mesoporous organosilicate we demonstrate the role of crystallographic orientation of Si substrate in directing the growth of material with highly ordered 3D pore architecture.

8:30 AM - 9:00 AM
PRE-NUCLEATION CLUSTERS AS SOLUTE PRECURSORS IN PHASE SEPARATION
Invited
Denis Gebauer
University of Konstanz, Konstanz, Germany

Contrary to the notion of classical nucleation theory, the occurrence of stable clusters in aqueous solution prior to nucleation has been demonstrated for various minerals. While it is classically assumed that ion-by-ion growth of un- and metastable species is central to nucleation events, phase separation via stable pre-nucleation clusters is based upon aggregation of larger nanoscopic entities. This process initially yields amorphous nanoparticles, and represents a crystallization pathway, which has been studied in the most abundant biominerals, calcium carbonate and calcium phosphate, in particular. Utilizing computer simulations, it has been proposed that pre-nucleation clusters are highly dynamic and liquid-like chains of alternating kations and anions, which lay the foundation to an initial nanoscopic liquid-liquid separation. In case of CaCO₃, spectroscopic analyses of amorphous intermediates formed from these precursors have evidenced distinct short-range structural features. This observation can be discussed in terms of amorphous polymorphism, which may be central to the yet unresolved question of crystalline polymorph selection. In this talk, a general overview of the pathway of phase separation via pre-nucleation clusters is presented, highlighting the latest findings in the field.

9:00 AM - 9:30 AM
INSIGHTS FROM SIMULATION FOR CALCIUM CARBONATE NANOPHASES, CRYSTALS AND NUCLEATION
Invited
P. M. Rodger, Aaron R. Finney, Yuriy G. Bushuev
University of Warwick, Coventry, United Kingdom

A great deal of debate has surrounded the nucleation and growth of calcium carbonate from solution over the past decade, with a number of pathways to crystallisation proposed, including thermodynamically stable pre-nucleation clusters, dynamical polymer-like aggregates of hydrated ions, and a metastable dense liquid phase. Yet the option of classical growth of crystalline phases from constituent ions and ion pairs has not been ruled out. In this talk we present the results of a computer simulation investigating a range of calcium carbonate species found during the initial stages of biomineral formation. Using a combination of molecular dynamics, metadynamics, adiabatically biased molecular dynamics and umbrella sampling, we examine the relative thermodynamic stability of various proposed precursor states, and their relation to both hydrated amorphous calcium carbonate and crystalline polymorphs.

9:30 AM - 10:00 AM
A CLASSICAL VIEW ON A NONCLASSICAL CRYSTALLIZATION PROCESS: THE PILP-PROCESS REVISITED.
Invited
Stephan E. Wolf
Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

The polymer-induced liquid-precursor (PILP) process falls within the so-called nonclassical crystallization processes which embrace all crystallization pathways which cannot be explained straightforwardly by means of the pertinent theories of crystal nucleation and growth as given since the twenties of the last century. The increasing number of publications reporting nonclassical crystallization processes seem to shake our understanding of crystallization to the very foundations. Prominent examples for such processes are the formation of highly ordered mosaic crystals with a negligible angle spread by oriented-attachment or the formation of
prenucleation clusters in undersaturated mineral solutions. The third member of this nonclassical triumvirate is clearly the PILP process which stands out from other precipitation reactions with its complexity and by its potential for morphosynthesis of crystalline materials. Triggered by mere addition of tiny amounts of small polyelectrolytes, classical nucleation of a solid crystalline phase is suppressed promoting the formation of a liquid-condensed phase of mineral precursor. This unusual transient mineral precursor phase becomes the crucial agent changing the entire character of the process. The route to the formation of a solid phase runs no longer via classical nucleation. Instead, a pseudomorphic solidification process takes places; the transient and highly hydrated liquid-condensed mineral precursor phase dehydrates, solidifies and eventually crystallizes under retention of a non-equilibrium morphology. Although the PILP process may represent a potent method to generate crystalline materials with non-equilibrium morphologies, its mechanismal foundations seem still enigmatic. In order to tackle this problem, we will show that we have to approach the nonclassical PILP process in a new, less holistic way. By focusing on individual step of the PILP process separately, we see that the individual steps of the process are less nonclassical as initially thought: each step can be reconciled with established and thus classical theories. However, the complexity and the essence of the PILP process is based on the fact that the individual classical processes do not occur uncoupled from the other processes but the overlap in time affecting each other. This intimate entanglement of classical processes gives rise to the apparent nonclassicity of the PILP process. Therefore, we claim that for a full understanding of the PILP process and for unlocking of its full morphosynthetic potential, a reductionistic, “deconstructive” approach will be essential.
Thursday, August 6, 2015
8:00 AM - 10:00 PM

OMVPE of Compound Semiconductors for Optoelectronics 1

Location: Gallatin
Session Chair(s): Jeff Cederberg

8:00 AM - 8:20 AM
ENHANCING THE QUANTUM EFFICIENCY OF III-V NANOWIRES
Hoe Tan¹, Nian Jiang¹, Patrick Parkinson¹, Sudha Mokkapati², Dhruv Saxena¹, Qiang Gao¹, Chennupati Jagadish¹
¹The Australian National University, ACT, Australia; ²The University of Manchester, Manchester, United Kingdom

III-V semiconductor nanowires have excellent characteristics which can potentially be exploited for future optoelectronic and electronic devices. However, due to their large surface-to-volume ratio and the high density of surface states that can act as non-radiative recombination centers, the quantum efficiency of nanowires can be severely degraded. Hence it is important to enhance the quantum efficiency of nanowires for device applications.

The quantum efficiency of semiconductors is defined as \( \frac{\text{tau}_\text{nr}}{\text{tau}_\text{nr} + \text{tau}_\text{r}} \), where \( \text{tau}_\text{nr} \) and \( \text{tau}_\text{r} \) are the non-radiative and radiative lifetimes, respectively.

One way to increase quantum efficiency is to increase \( \text{tau}_\text{nr} \). Since \( \text{tau}_\text{nr} \) is predominantly related to carrier recombination at defect/impurity sites and surface states, this quantity can be increased by improving the material quality and passivating the surface. In this work we investigate the growth regimes that result in high quality Au-catalyzed GaAs nanowires. Furthermore, by investigating the growth conditions of an AlGaAs shell to passivate the GaAs nanowire surface, the quantum efficiency can be markedly increased leading to the demonstration of room temperature lasing from these nanowires.

An alternate way to increase the quantum efficiency is to reduce \( \text{tau}_\text{r} \). We use two different cavity designs to induce plasmonic coupling between the metals and core-shell nanowires to shorten their radiative lifetime. One design based on silver nanoparticles is able to affect only the AlGaAs shell, whereas an omega-shaped Au cavity can affect both the AlGaAs shell and GaAs core. This research is supported by the Australian Research Council. The Australian National Fabrication Facility is acknowledged for access to some of the facilities used in this work.

Fig. 1 Schematic of the omega-shaped cavity (left), cross-sectional TEM image of the nanowire enclosed by a layer of Au (middle) and room temperature photoluminescence spectra of the bare nanowire and nanowire with omega-shaped cavity (right). Scale bar in the middle image is 50 nm.

8:20 AM - 8:40 AM
EFFICIENT YELLOW AND GREEN EMITTING INGAN / GAN NANOSTRUCTURED QW MATERIALS AND LEDS
Yoshitake Nakajima, Yenting Lin, Daniel P. Dapkus
University of Southern California, Los Angeles, CA

Efficient green emitting LEDs and monolithic white light emitting LEDs require the extension of the range of efficient light emission in the GaN / InGaN materials system. We demonstrate high efficiency green and yellow light emitting multiple quantum well (MQW) structures grown on GaN nanostripe templates. The structures show promise for realizing high efficiency phosphor - free white LEDs. The nanostripe dimensions range from 100 nm to 300 nm and have separations that range from 300 nm to 1 micron. Such small lateral dimensions are chosen to promote the elimination of threading dislocations from the structures. Nanostrips with various nonpolar and semi polar surfaces are grown with selective area growth on e-beam lithography patterned c-plane GaN where the mask openings are oriented between the [10-10] and [11-20] directions. The MOCVD growth conditions strongly affect surfaces expressed in the GaN nanostripe patterns. With stripes are aligned along the [10-10] and [11-20] directions, the sidewalls can be controlled to be nearly vertical or inclined and intersecting. Both shapes were examined. MQWs are grown on these different stripes. Photoluminescence (PL) measurement shows that MQWs grown on stripes with (10-11) surfaces and triangular shape emit the longest peak wavelength and have the best surface stability. Gas phase and surface diffusion of the III reagents can affect the growth rate and compositions of the MQWs grown on stripes with different dimensions and spacing, placing a premium on uniform patterning and deposition. Efficient PL emission peak wavelengths as long as 570 nm are realized on the triangular stripes with (10-11) surfaces by optimizing the MQW growth conditions for long wavelength emission. Power dependent PL measurements show linear response over more than three orders of magnitude of excitation power, indicating high radiative recombination efficiency.

Cathodoluminescence mapping shows both the peak wavelength and intensity increase from the bottom to the top of the stripes. We attribute the trend to higher degree of strain relaxation and out-coupling of light near the tip of the stripes. LED structures that utilize MQWs grown on nanostripes with (10-11) surfaces were fabricated to further demonstrate the viability of the approach.

- The quantum efficiency of nanowires is enhanced by improving material quality and passivating the surface.
- Quantum efficiency is increased by reducing the radiative lifetime through cavity designs.
- Green and yellow light emitting MQW structures are demonstrated on GaN nanostripe templates.
- Efficient PL emission is achieved with optimized growth conditions.
- Cathodoluminescence mapping verifies the increase in peak wavelength and intensity.
8:40 AM - 9:00 AM
GROWTH AND CHARACTERIZATION OF AlGaN PIN ULTRAVIOLET AVALANCHE PHOTODIODES GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION
Jeomoh Kim1, Mi-Hee JI1, Theeradetch Detchpoom1, Russell Dupuis1, Ashok Sood1, Nabir Dhar1
1Georgia Institute of Technology, Atlanta, GA, 2Magnolia Optical Technologies, Wobum, MA, 3Night Vision Sensors and Electronic Division, Ft. Belvoir, VA

Growth and Characterization of AlGa0.9N Ultraviolet Avalanche Photodiodes Grown by Metalorganic Chemical Vapor Deposition

The realization of high-performance AlGaN-based UV-APDs is still challenging mainly due to difficulties in growing high-quality AlGa0.9N layers on lattice-mismatched foreign substrates such as sapphire and SiC. The AlGa0.9N layers grown by strained heteroepitaxay have high density of crystalline defects, resulting in compromised performance characteristics. In this study, AlGa0.9N p-i-n (PIN) UV-APD structures (x=0-0.05) having avalanche gain greater than 105 are demonstrated by using “free-standing” (FS) n-type GaN substrates having low dislocation densities (< 1x107 cm-2). In addition, a strain management layer in n-type layers is introduced as a way to further minimize additional crystalline defects resulting from the lattice mismatch between substrate and the active layer.

The epitaxial layer structures of AlGa0.9N PIN UV-APDs were grown on a c-axis n-type FS-GaN substrate by a metalorganic chemical vapor deposition system. The top-illuminated APD structure grown in this study is shown in Fig. 1(a). To improve crystalline and structural quality, the growth and doping conditions for each epitaxial layer in the device structure were optimized by modifying growth parameters. The step-graded layers from n-GaN:N to n-AlGa0.95Ga0.05N:N:Si were introduced instead of thick n-AlGa0.95Ga0.05N:S:S layers as a strain management scheme for limiting additional defect density as well as crack-free growth. The active area of these APDs, as shown in Fig. 1(b), was fabricated into circular mesas with various diameters from 30 μm to 70 μm by using standard photolithography and inductively coupled plasma etching, followed by SiO2 passivation using plasma-enhanced chemical vapor deposition. Fig. 1(c) exhibits reverse-bias I-V characteristics of a UV-APD having a mesa diameter of 30 μm. Under the illumination with λ~280 nm for photocurrent, a maximum avalanche gain > 105 was achieved at a reverse bias of 102 V and no microplasmas was visually observed. The growth and characterization of the AlGa0.9N PIN UV-APDs will be further discussed in detail.

FIG. 1: (a) schematic diagram of epitaxial layer structure, (b) top-view image of devices measured by SEM, and (c) reverse-bias I-V characteristics of an AlGaN PIN UV-APD.

9:00 AM - 9:20 AM
MOVPE GROWTH OF GA(PASBI)/GAAS AND GA(NASBI)/GAAS AT LOW TEMPERATURES FOR OPTOELECTRONIC APPLICATIONS
Lukas Nattermann
Philips Universitat Marburg, Marburg, Germany

Dilute bismide Ga(PasBi) and Ga(NasBi) based structures are promising candidates for highly efficient optoelectronic applications, like 1eV layers in multi junction solar cells or laser diodes that emit in the infra-red region. Since Bi has a larger covalent radius than As, while the covalent radius of P is smaller and Bi has a larger impact on the band structure than P, the band gap in both materials can be tuned independently from the lattice constant. A strain free crystal could be an asset, since investigations on the growth of Ga(AsBi) have shown that the growth of bismide containing materials is very challenging, due to the larger Bi atoms, especially when using metalorganic vapour phase epitaxy (MOVPE), as very low growth temperatures are required in order to incorporate a significant amount of Bi. For the growth of Ga(AsBi) we have already seen that the interaction between the metalorganic molecules, as well as between the molecules and the growth surface, cannot be neglected and for example leads to a decreasing growth rate when group V partial pressures are changed.

In this study, the influence of adding P and N to Ga(AsBi) is investigated and the influence of strain and gas phase composition on the resulting composition is of interest. The addition of P and N should bring more information about the growth process and lead to a better understanding of the complex incorporation characteristics of Bi in III/V material systems. Different Ga(AsBi), Ga(PAs), Ga(PASBi) and Ga(NAsBi) layers are grown at 400°C on exact GaAs (001) substrate using Triethylgallium(TEGa), Tertiarybutylarsine (TBAs), Tertiarybutylphosphine (TBP), Trimethylbismuth (TMBi) and unsymmetric Dimethylhydrazine (UDMHy). The crystalline quality, growth rate and Bi incorporation were investigated using HR-XRD, TEM, SIMS, SEM and AFM in order to understand the growth of the dilute bismide material systems. We will show that not only strain is a limiting factor for Bi incorporation but also the gas phase composition and related
interactions between molecules and the growth surface are important for the understanding of the growth process and to grow high quality crystals in a wide range of band gaps.

9:20 AM - 9:40 AM
ORGANOMETALLIC VAPOR PHASE EPITAXY (OMVPE) OF HIGH BI CONTENT GA(ASPBI) "BULK" LAYERS
Kamran Forghani, Maria Losurdo, Yingxin Guan, April Brown, Guangfu Luo, Adam Wood, Susan Babcock, Luke Mawst, Dane Morgan, Thomas F. Kuech

1 Materials Research Science & Engineering Center, University of Wisconsin, Madison, WI; 2 Institute of Nanotechnology, CNR, Bari, Italy; 3 Materials Science & Eng. Dep., University of Wisconsin, Madison, WI; 4 Electrical and Computer Eng., Duke University, NC; 5 Electrical and Computer Eng. Dep., University of Wisconsin, Madison, WI; 6 Chemical and Biological Eng. Dep., University of Wisconsin, Madison, WI

The growth of GaAs$_{1-y}$Bi$_y$ epitaxial layers with acceptable optical properties for device applications remains a challenge. The Bi solubility is a function of the strain state of the alloy besides other growth parameters. Bi incorporation becomes energetically more favorable, if the epitaxial film is under tensile strain [1]. In such films, the incorporation of Bi compensates the existing strain, reducing the overall strain in the epitaxial layer. This scenario can be achieved by the addition of Bi to a pseudomorphic film of GaAs$_{1-y}$Py film grown on a GaAs substrate.

We report on the growth and characterisation of quaternary GaAs$_{1-y-z}$P$_z$Bi$_y$ by metal-organic vapour phase epitaxy (MOVPE). This materials system allows simultaneous tuning of lattice constant and band gap energy, $E_g$, over a wide range for near- and mid-IR optoelectronic applications, by adjusting $y$ and $z$ in GaAs$_{1-y-z}$P$_z$Bi$_y$. According to our growth studies, the higher Bi source fluxes (TEBi) result in a growth rate reduction. This growth rate decrease with the Bi source flux was attributed to the relatively high life time of Bi precursor's species, blocking the surface sites for the absorption and dissociation of group III source (here TEGa).

The theoretical band gap energies were calculated using density function theory (DFT) with the composition determined by electron microprobe measurements. The band gap energies of the grown films were extracted from ellipsometric measurements. The measured $E_g$ of the films shows a good agreement with the calculated $E_g$ from the DFT calculations. Such ellipsometric evaluations also indicate $E_g$ as well as the Urbach tail of the GaAs$_{1-y-z}$P$_z$Bi$_y$ films originated from alloy disorder in atomic scales, and effectively reducing the energy of the "absorption edge" of such films, $E_t$ (Fig. 1-left). Accordingly, an increase of Bi/P content (reduction of As content) in GaAs$_{1-y-z}$P$_z$Bi$_y$ films results in longer Urbach tails (larger "$E_g$-$E_t$"), as shown in Figure 1-right. Although two sets of samples were investigated (grown at different temperatures: 380$\degree$C vs. 420$\degree$C), the "$E_g$-$E_t$" values are independent of the growth temperature of the epitaxial films. Thus, it can be concluded that the increase of Bi and P content in the GaAs$_{1-y-z}$P$_z$Bi$_y$ films in order to maintain the (near) lattice match conditions and tune the fundamental band gap energy induces compositional/structural disordering.


* Scheme in Figure 1-left adapted from ISRN Condensed Matter Physics, 2012, 10 (2012)

9:40 AM - 10:00 AM
N-INCORPORATION IN GAAS USING A NOVEL GROUP-V-PRECURSORS WITH NO DIRECT C-N-BOND
Eduard Sterzer
Philipps-Universität Marburg, Marburg, Germany

III/V semiconductors containing small amounts of Nitrogen are discussed in the context of solar cell and laser applications. Unintended C- incorporation during growth can hamper the performance of the devices. C-uptake during MOVPE (metal organic
vapour phase epitaxy) growth either stems from the N-precursor or from the group III-sources, where the N - due to the high strength of the C-N-bond - leads to the incorporation of C from the organic rest groups. Furthermore, in the growth of these materials, a large excess of the N-precursor has to be offered in the gas phase in order to incorporate only small amounts of N. Conventionally, UDMHy (unsymmetric1,1-dimethyl hydrazine) is used as a N-precursor in MOVPE growth of dilute nitrides. We synthesized and purified a novel precursor (Ditertbutyl-arsano-amine: DTBAA) for use in dilute nitride growth. This precursor has the advantage that no C-N bond exists in the molecule, which could reduce the C-incorporation and increase the efficiency of semiconductor devices. We used this molecule - together with TEGa (triethylgallium) and, in some experiments, also with TBAs (tertiarybutylarsine) - in low temperature growth of Ga(NAs) on GaAs substrates. We observe an extremely efficient N-incorporation from this molecule. The layer structures grown using DTBAA exhibit high structural quality, as shown in figure 1. Pendellösung fringes in high resolution X-ray diffraction (HR-XRD) are resolved to high order and surface morphologies (as measured by atomic force microscopy (AFM)) are smooth. Also, the quantum well structures exhibit room temperature photoluminescence at the wavelength consistent with the N-content measured from XRD.

This work will present a systematic study of incorporation characteristics of N from this novel precursor. In addition, C-impurity levels will be compared to those known from MOVPE growth using UDMHy.

Fig. 1: HR-XRD profile of a Ga(NAs) sample on the left and an AFM image of a Ga(NAs) surface.
MOVPE GROWTH OF LASER STRUCTURES FOR HIGH-POWER APPLICATIONS AT DIFFERENT AMBIENT TEMPERATURES

Frank Bugge, Andre Maßdorf, Paul Crump, Carlo Frevert, Steffen Knigge, Hans Wenzel, Götz Erbert, Markus Weyers
Ferdinand-Braun-Institut, Berlin, Germany

GaAs-based high power diode lasers are efficient sources of optical energy, and are in wide use in industrial applications, either directly or as pump sources. Increased power is required to enable new applications and to reduce cost in $/W. The wide range of applications leads to very different operating conditions, for example 800 nm lasers optimized for 50°C package temperature are needed for use in printing. In contrast, 9xx nm lasers optimized for ~200K package temperature promise enhanced efficiency and powers, as needed for high energy pumping applications. Here we discuss how the design of epitaxial layer structures must be adapted to deliver high powers at the two extremes (+50°C and -70°C.)

Diode lasers emitting between 730 nm and 1060 nm typically consist of Al,Ga,As waveguide and cladding layers with x>0.3. Improved performance at high temperature requires increased barriers against thermally-promoted carrier escape from the active region which can be achieved by using high band-gap (Al)GaInP waveguide layers. Therefore, a series of structures were grown by MOVPE, with Al0.65Ga0.35As, GaInP or AlGaInP waveguide layers and (consistent) Al0.7Ga0.3As cladding layers. A critical point for such structures is the formation of high quality hetero-interfaces between (Al)GaInP and AlGaAs. The highest performing vertical design enables single emitters with 130 µm stripe width to deliver peak optical output power of 16 W at 50°C. 1 cm wide laser bars containing 19 such emitters (30% filling factor) emit a maximum output power of 100 W under the same conditions, limited by rollover.

At the other extreme, operating at a package temperature of 200K strongly suppresses carrier escape, allowing layers with low x to be used. Al,Ga,As layers with low x have higher mobility, leading to lower electrical resistance and hence potentially higher peak efficiency. A series of device structures with different Al-contents in the waveguide layer (x = 0⋯17.5%) was therefore produced, and the dependence of threshold current on temperature is shown in Fig.1 for example devices with 100 µm stripe width and 4 mm cavity length. Threshold tends to a common value ~400 mA for x>1% as temperature tends to 200K due to suppression of carrier escape, supporting the use of low x at low temperatures. Building on these studies, 1-cm laser bars with high fill factor (70%) were fabricated using low-temperature-optimized designs. These bars reached an output power of 2 kW (0.2 ms, 10 Hz) at 203K package temperature, limited by available current.
DEVELOPMENT OF STRAIN-COMPENSATED INGAAS/GAASP QW FOR OPTICALLY PUMPED VERTICAL EXTERNAL CAVITY SURFACE EMITTING LASERS AT 1178 NM

Jeffrey G. Cederberg1, Darrell L. Alliman1, Gregory M. Peake1, Alexander R. Albrecht2, Shawn Hacket2, Shawn Hacket2, Zhou Yang2, Mansoor Sheik-Bahae2

1Sandia National Laboratories, NM, 2University of New Mexico, Albuquerque, NM

The extension of InGaAs quantum wells (QW) on GaAs to longer emission is a challenging problem that has been considered extensively in previous investigations. The challenge is managing the strain introduced as the amount of indium increases to achieve the target wavelength. Our effort focused on development of a sodium guidestar for astronomical adaptive optics, which required the development of a frequency doubled 1178 nm laser to pump sodium atoms in the mesosphere. This talk will focus on efforts to develop 1178 nm InGaAs QWs and their incorporation into vertical external cavity surface emitting lasers (VECSELs).

Our efforts utilized low pressure (60 Torr) MOVPE for growth on GaAs substrates using a high-speed rotating disk chamber. The growth used hydrides and methyl-based metal-organics. The V/III ratio and growth temperature were varied to achieve improvements in room temperature photoluminescence response. The structure investigated during development consisted of six single quantum wells separated by lambda/2 spacer layers. Achieving 1178 nm requires compositions near In0.4Ga0.6As, which necessitates strain compensation to avoid dislocation injection that leads to optical degradation. Our strain balancing approach used GaAs0.96P0.04 over the whole spacer thickness. We identified that low growth temperatures (520°C) are necessary to observe luminescence. As the temperature is lowered the effective V/III ratio decreases because less hydride is decomposed. This requires higher inlet V/III ratios, approaching 400. Low temperature/high V/III QWs were incorporated into VECSEL structures, but lasing was not observed. We speculate the reason was due to the degraded interface associated with the low temperature growth of a thick spacer layers. Typically GaAs layers have RMS roughness below 1 nm, while 1178 nm InGaAs/GaAsP structures have RMS roughness exceeding 3 nm. The high roughness was mitigated by utilizing a two-temperature growth process, where the majority of the spacer is grown at 650°C, and the temperature is lowered only for the InGaAs QW. This two-temperature approach allowed the RMS roughness to be reduced to 1 nm. VECSELs using the two-temperature approach perform as expected, generating powers in excess of 11 W, only limited by the available pump power, with slope efficiencies of 32%, with respect to the absorbed pump power. We have demonstrated frequency doubling using this approach.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

SENSITIVITY OF QUANTUM CASCADE LASER PERFORMANCE TO THICKNESS AND DOPING VARIATIONS
Dominic F. Siriani, Christine A. Wang, Joseph P. Donnelly, Leo J. Missagga, Michael K. Connors, Daniel R. Calawa, Daniel McNulty, Tobias S. Mansuripur, Federico Capasso

1. MIT Lincoln Laboratory, Lexington, MA; 2. Harvard University, Cambridge, MA

Unlike most competing technologies, quantum cascade lasers (QCLs) are coherent optical sources capable of room temperature, continuous wave operation over a broad bandwidth in the mid- and long-wave infrared (MWIR and LWIR) spectral regions. This aspect makes them appealing for applications in infrared countermeasures, spectroscopy, chemical and biological sensing, and free-space optical communications. The flexible wavelengths of QCLs are achievable because the optical transition energy is determined by the energy separation of subband states in the conduction band of a coupled quantum well structure. The energy level separation is determined by the thickness of the many quantum wells and barriers in the structure, which typically can number 20-25 layers with some layers only a few monolayers thick. As such, there is potential for unintentional growth variations to produce significant differences between the intended and physically realized QCL structure.

In this work, we report on a study of the effects of intentional thickness and doping variations on QCL performance. A baseline LWIR AlInAs/GaInAs/InP QCL structure was used as the control, and variations to the structure including a ~5% longer (shorter) QCL period, complementarily thicker and thinner wells and barriers (±0.05 nm), thicker (thinner) injection barriers (±1 nm), injector doping levels, etc. were investigated. AlInAs/GaInAs/InP QCL structures were grown by OMVPE at 625°C using methyl-based precursors, AsH3, PH3, and SiH4 as n-type dopant. The periodicity of grown structures was verified by x-ray diffraction measurements. Standard photolithography was used to fabricate ridge lasers and mesa test structures. Power-current-voltage characteristics were measured, and the emission wavelength was determined by electroluminescence.

The measured QCL data had very similar trends to those predicted by an in-house QCL model. It was found that absolute changes to the QCL period had a very small effect on emission wavelength (wavelength/period change < 10 nm/Å), whereas the complementary thickness changes between the wells and barriers had a large effect (wavelength/thickness change = 550 nm/Å). The threshold voltage also changed with these variations and generally agreed well with the model. Additional QCL structure modifications are ongoing and will be presented. We will show through modeling and experiments that intentional structure variations can have largely different magnitudes of effect on QCL performance.

This work was sponsored by Assistant Secretary of Defense for Research and Engineering (ASD R&E) under Air Force Contract FA8721-05-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the United States Government.

11:30 AM - 11:50 AM
MID-INFRARED QUANTUM CASCADE LASERS FABRICATED BY NON-SELECTIVE REGROWTH AND CHEMICAL POLISHING
University of Wisconsin, Madison, WI

Objectives: Develop fabrication processes for realizing buried heterostructure (BH) quantum cascade lasers (QCLs) for efficient heat removal and optical mode control. Such techniques allow for monolithic phase-locking of multiple QCLs for coherent power scaling.

Method: For the realization of BH-QCLs, we employ non-selective regrowth of Fe:InP via OMVPE, followed by planarization using chemical polishing. Through the use of a non-selective regrowth approach, the effect of the dielectric mask on the regrown-InP morphology (observed for selective regrowth) can be completely removed. After the regrowth, the CP step uniformly polishes down the excess regrown InP material, and hence the entire device surface area is nearly planarized, which is particularly crucial for ep-side down laser-chip mounting.

We have previously reported the realization of resonant-weak coupling of QCLs by selective regrowth of interelement layers in curved trenches, defined by dry and wet etching, which, in turn, has provided in-phase-mode operation to 5.5 W front-facet emitted power in a near-D.L. far-field beam pattern, with 4.5 W in the main lobe [1]. Since the interelement layers are grown selectively using a SiN mask, these regrown layers have curvature and the critical layer dimensions are difficult to control. Here we report a refined fabrication process to produce such arrays with a planar geometry utilizing the non-selective regrowth of Fe:InP after defining the interelement trenches, followed by a chemical polishing (CP) step to planarize the surface. After CP planarization, the interelement layers (in this case, InGaAs and InP) are regrown over the entire surface. Finally, we pattern and selectively etch the interelement layers from the array element regions, followed by an InP regrowth over the entire surface.

Results: Due to better heat dissipation, the fabricated 4.75 μm-emitting single element QCLs exhibit a ~ threefold enhancement in maximum output power under CW operation at room temperature compared to that from lasers without the regrown InP.

The fabrication process for phase-locked arrays of QCLs employing weak-wave coupling have also been realized. The planarized InGaAs/InP interelement regions allow for significantly improved control over the array geometry and the critical dimensions. The attached figure shows an SEM cross-sectional image of a three-element phase-locked array of QCLs.

Conclusions: A non-selective OMVPE growth and chemical polishing process has been developed which can be utilized for the fabrication of BH mid-infrared QCLs and large-emitting-aperture, closely-packed arrays with planarized geometry, for coherent-power scaling.

ENHANCEMENT OF GaAs VGF PROCESS USING A HEATER MAGNET MODULE
Christiane Frank-Rotsch, Natasha Dropka, Alexander Glacki, Uta Juda
Leibniz-Institute for Crystal Growth, Berlin, Germany

The development of vertical gradient freeze (VGF) growth process focuses on the increase of process efficiency by a reduction of the production costs with simultaneous improvement of the crystal quality. For process enhancement, an exact and permanent control of the melt flow is of crucial importance, which can be easily provided by a traveling magnetic field (TMF). To meet this technological and scientific challenge, various strategies are feasible. We investigated e.g. an increase of crystal size, simultaneous crystallization in multi crucible furnace and an increase of growth rate. In our investigation a KRISTMAG internal heater-magnet module (HMM) was positioned sidewise around the crucible and was supplied by a combination of DC and AC for a coupled generation of thermal and magnetic fields. A wide range of electromagnetic parameters was available for process optimization. The influence of the magnetic parameters on the GaAs single crystals growth in the HMM was be discussed with respect to the feasibility of process enhancement. The key aspect of the investigation was the well-defined control of the solid/liquid interface bending in the grown VGF crystals. Therefore, a numerous preliminary 3D CFD simulations of the whole furnace were inevitable. Results, both numerical and experimental, showed that the downward-directed Lorentz forces generated near the crucible wall if properly adjusted enabled a significant decrease of the concavity of the solid-liquid interface. A reduction of the deflection by about 30% in comparison to crystals grown without TMF was obtained at nearly doubled crystal growth rate.

DETACHED BRIDGMAN GROWTH OF GERMANIUM AND GERMANIUM-SILICON CRYSTALS UNDER MICROGRAVITY
Invited
Arne Croell¹, Adam Hess¹, Jan Zähringer¹, Tina Sorgenfrei¹, Alexander Egorov², Alexander Senchenkov²
¹University of Freiburg, Freiburg, Germany, ²NIISK - Research and Development Institute for Launch Complexes, Moscow, Russian Federation

In 2014, four microgravity (µg) experiments on the Bridgman growth of Ge and Ge-Si under different convective conditions were performed on the FOTON M4 unmanned satellite. Three of the experiments used Ga-doped Ge. They employed purely diffusive conditions, a flow regime dominated by a rotating magnetic field, and an axial vibration regime, respectively. The first two of the experiments also showed detached growth. The fourth experiment used a Ge-Si mixed crystal and investigated primarily detached growth, as shown in the image below. Results of these µg experiments will be presented and compared to 1g reference experiments with respect to segregation and structural defects.
SHAPE EVOLUTION OF DETACHED BRIDGMAN CRYSTALS GROWN IN MICROGRAVITY

Martin Volz, Konstantin Mazuruk
1NASA MSFC, Huntsville, AL, 2University of Alabama Huntsville, Huntsville, AL

Detached (or dewetted) Bridgman crystal growth defines that process in which a gap exists between a growing crystal and the crucible wall. In microgravity, the parameters that influence the existence of a stable gap are the growth angle of the solidifying crystal, the contact angle between the melt and the crucible wall, and the pressure difference across the meniscus. During actual crystal growth, the initial crystal radius will not have the precise value required for stable detached growth. Beginning with a crystal diameter that differs from stable conditions, numerical calculations are used to analyze the transient crystal growth process. Depending on the initial conditions and growth parameters, the crystal shape will either evolve towards attachment at the crucible wall, towards a stable gap width, or inwards towards eventual collapse of the meniscus. Dynamic growth stability is observed only when the sum of the growth and contact angles exceeds 180°.

GROWTH OF INSB AND INI CRYSTALS ON EARTH AND IN MICROGRAVITY

Aleksandar G. Ostrogorsky, Alexei Churilov, Martin Volz, Vladimir Riabov, Lodewijk van den Berg
1IIT, Chicago, IL, 2RMD, Watertown, MA, 3MSFC, NASA, Huntsville, AL, 4Constellation Technology Corporation, Largo, FL

During the past 40 years, dozens of semiconductor crystal growth experiments have been conducted in the space laboratories. The subsequent analysis of the space-grown crystals revealed (i) that weak convection existed in virtually all melt-growth experiments, (ii) de-wetting significantly reduced the level of stress-induced defects, (iii) particularly encouraging results were obtained in vapor-growth experiments. In 2002, following a decade of ground based research in growing doped Ge and GaSb crystals, a series of crystal growth experiments was performed at the ISS, within the SUBSA (Solidification Using a Baffle in Sealed Ampoules) investigation. Te- and Zn-doped InSb crystals were grown from the melt. The specially designed furnace provided side-view to the melt, precise seeding measurement of the growth rate.

At present, under sponsorship of CASIS (Center for the Advancement of Science in Space, www.iss-casis.org) we are conducting ground-based experiments with indium mono-iodide (InI) in preparation for “SUBSA II” ISS investigation, planned for 2017. The experiments include: i) Horizontal Bridgman (HB) growth and ii) Vapor Transport (VT) growth. Finite element modeling is conducted, to optimize the design of the flight ampoules, for vapor and melt growth.
ADVENTS ON THE LARGE DIAMETER SiC SUBSTRATE GROWTH AT II-VI

Invited

Varatharajan Rengarajan, Xueping Xu, Avinash Gupta, Ping Wu, Mark Ramm, Illya Zwieback, Gary Ruland
Advanced Materials Group, II-VI, Inc, Pine brook, NJ

Affordable, high quality SiC substrates are very desirable for a variety of new technologies including GaN based lighting, RF, and high-power electronics. Large diameter SiC single crystals are grown at II-VI by the seeded sublimation technique. II-VI manufactures up to 150 mm diameter substrates of two types: vanadium doped semi-insulating and nitrogen doped n-type. This presentation is an update on the development of large diameter, high quality SiC substrates. The growth process incorporates special elements aimed at achieving uniform sublimation of the source, stable growth interface, steady growth rate, uniform doping and reduced presence of background impurities. SiC single crystals grown by sublimation exhibit relatively high dislocation densities and often contain a network of slightly misoriented grains. Defect data will be presented on wafers that have been characterized by etch pit density and X-ray rocking curves and topography. Resistivity was characterized by an eddy current measurement for conducting and capacitive based measurement for semi-insulating substrates. Using these methods a comparison of progress will be provided. We have achieved stacking fault free, low dislocation density micro pipe free n-type substrates. Typical total dislocation density is $4 \times 10^3$ cm$^{-2}$, TSD density is $\sim 7 \times 10^2$ cm$^{-2}$, and typical BPD density is $3 \times 10^2$ cm$^{-2}$ in 150mm substrates. For semi-insulating wafers we have achieved resistivities in excess of $1 \times 10^9$ ohms$\cdot$cm. The current quality of Si and n+ crystals grown at II-VI will be summarized.

CHARACTERIZATION OF CdZnTe SINGLE CRYSTALS GROWN UNDER DIFFERENT Cd OVERPRESSURES

Ouloide Y. Goue¹, Raghothamachar Balaji¹, Michael Dudley¹, Ching-Hua Su²
¹Stony Brook University, Stony Brook, NY, Materials and Process Laboratory, Engineering Directorate, NASA/ Marshall Space Flight Center, Huntsville, AL

Cadmium Zinc Telluride (CdZnTe) single crystals are the material of choice for the room temperature detection of γ-rays and hard x-rays in security, medical and space applications. Obtaining high quality single crystal is a challenge in the growth of CdZnTe crystals, and the high density of structural imperfections limits the detection power of CdZnTe-based detectors and their energy resolution. Further a critical requirement for CdZnTe detector applications is high electrical resistivity to reduce the bulk leakage current. By growing CdZnTe under controlled Cd overpressure, high resistivity has been reproducibly obtained. However, it is also necessary to obtain a thorough understanding of this growth modification on the structural quality of the crystals grown. In this study, the influence of Cadmium (Cd) overpressure on the growth of CdZnTe single crystals by vertical directional solidification (Bridgman technique) method is evaluated. To that end, boules with different Cd overpressures were grown. Axial and transverse slices cut from the boules and polished were investigated using a combination of synchrotron white beam x-ray topography (SWBXT), Infrared spectroscopy and double axis x-ray diffraction. Preliminary SWBXT results reveals the presence of twinning and a uniform distribution of a network of subgrain boundaries and dislocations. Infrared mapping revealed a high density of Te inclusions, which decorated twin boundaries and aligned along subgrain boundaries and dislocations. The Te inclusions have circular and triangular shapes, and their size is between 10 to 60µm. The Te inclusions will be quantified in term of their shape, size and density as function of Cd over-pressure. Further investigations of more samples are underway, and double axis x-ray diffraction will be carried out for each sample to determine their overall quality. These results will shed light on the influence of Cd overpressure on the structural perfection of CdZnTe crystals.

Reference:

MATERIALS INNOVATION PLATFORMS: A NEW NSF MID-SCALE INSTRUMENTATION AND USER PROGRAM TO ACCELERATE THE DISCOVERY OF NEW MATERIALS

Invited

Sean L. Jones, Guebre X. Tessema, Tom Rieker
National Science Foundation, Arlington, VA

Recognizing the ever increasing complexity of materials research that requires the close collaboration of multidisciplinary teams who have access to cutting edge tools, the NSF Division of Materials Research (DMR) has established the Materials Innovation Platforms (MIP) program. MIPs will push the frontiers of energy, spatial, and time resolution by developing next generation technologies, as well as advance the capabilities of current state-of-the-art experimental tools and techniques. MIPs will embrace the paradigm set forth by the Materials Genome Initiative (MGI) and seek to substantially increase the rate at which new materials and new materials phenomena are discovered. The in-house research conducted in a MIP is transformational and focuses on a targeted materials grand challenge and/or technological outcome that address a national priority. The small in-house research team is comprised of experts in new materials development (materials growers, characterization experts, and theorists) who collectively advance the research through an iterative and tight knit collaboration wherein theory guides computational simulation, computational...
simulation guides experiments, and experiments further guide theory. In addition, MiPs dedicate 50% of their time and effort managing an open user facility that serves as a national resource providing access to existing instrumentation; MIP-developed instrumentation, methods, and techniques; and other resources such as data, codes, and samples. Lastly, these Platforms will serve as educational focal points for training the next generation of instrument developers and users. In response to the 2009 National Academy report, *Frontiers in Crystalline Matter: From Discovery to Technology*, the first MIP competition focuses on the growth of bulk and thin film crystalline inorganic materials of high priority in areas of national significance.
SYNTHESIS OF STABLE AMORPHOUS NUCLEI FROM IONIC LIQUIDS

Invited

Wolfgang Tremel¹, Michael Dietzsch¹, Sebastian Leukel¹, Aaron Gehl¹, Bastian Barton¹, Ute Kolb¹, Renee Siegel², Jürgen Senker²
¹Johannes Gutenberg Universität, Mainz, Germany, ²Universität Bayreuth, Bayreuth, Germany

The mechanisms by which amorphous intermediates transform into crystalline materials are still poorly understood. In order to test the viability and the limits of the classical crystallization, new model systems for crystallization are needed. Here we attempt to illuminate the formation of an amorphous precursor and its subsequent crystallization by investigating the crystallization process of calcium oxalate, a bimetallic widely occurring in plants. Amorphous calcium oxalate precipitated from aqueous solution is described as a hydrated metastable phase, as often observed during low-temperature inorganic synthesis and biominalerization. In the presence of water, amorphous calcium oxalate rapidly transforms into hydrated whewellite (monohydrate, CaC2O4-H2O). We have circumvented the problem of fast crystallization kinetics by synthesizing anhydrous amorphous calcium oxalate from a pure ionic liquid (IL-ACO). IL-ACO is stable under dry conditions even at elevated temperatures. It is obtained as non-agglomerated particles with diameters of 1-15 nm. When exposed to water, it crystallizes rapidly into whewellite.

Using this strategy, stable nanoparticles of other biomimerals such as calcium carbonate, calcium phosphate, or minerals such as calcium sulfate and zinc phosphate can be prepared. We demonstrate that by the synthesis of Mg-rich calcium carbonate. While biogenic calcites may contain considerable amounts of magnesium, the pathways leading to such high Mg contents are unclear. The synthesis of high-magnesian calcites in vitro is a challenge, because Mg-free aragonite, rather than calcite, is the preferred product in the presence of strongly hydrated Mg2+ ions. Nature bypasses this problem by choosing a reaction path via a Mg-rich amorphous precursor, which subsequently transforms to calcite. High-magnesian calcites (Mg content ≤20%) cannot be precipitated from aqueous solution because of the solubility of Mg2+ for high Mg2+/Ca2+ ratios, whereas amorphous calcium carbonate (ACC) with a high Mg content is not preserved because of the strong hydration of Mg2+. The synthesis from ionic liquids circumvents the problem of dehydration by precipitating Ca(1-x)MgxCO3 from weakly coordinating solvents. Ionic liquids with their tunable properties offer the possibility to create a weakly coordinating environment, where energetic differences in desolvation between the alkaline-earth cations are leveled. Our strategy yields the complete solid solution series Ca(1-x)MgxCO3 solution series and precludes crystallization of the ACC via a dissolution and reprecipitation route and enables investigating the role of bulk water in determining the product of Mg-ACC crystallization. Our findings also provide insight into the possible mechanisms of formation of biogenic high-magnesian calcites and indicate that precise control over the water activity may be a key element.

CORRELATION OF MINERALIZATION PATTERNS ON THE NANO- AND MICROMETER SCALE IN BONE

Roland Kroeger¹, Natalie Reznikov¹, Charlotte A. Boig¹, Teresa Roncal-Herrero¹
¹University of York, York, United Kingdom

The biocomposite bone has superior mechanical properties compared to the single components, which are largely due to the intricate combination of hydroxyapatite (HAp) based nanocrystals and collagen and the hierarchical structure of the resulting bone. One of the main challenges in understanding the correlation between the biogenic synthesis and assembly of this hard-sift matter composite lies in the complex manner in which this material is produced by the osteocytes. It is widely believed that collagen fibrils act as template for the formation of the hydroxyapatite mineral [1]. However, the actual mineral/organic arrangement patterns are disputed, where either a predominantly intrafibrilar or interfibrilar crystallization mechanism, respectively, are claimed [1,2]. To shed light on the relation between the nanoscale collagen/mineral structure and the micron scale assembly patterns we employed high-resolution electron microscopy in conjunction with µ-Raman spectroscopy to investigate the focused ion beam prepared samples extracted from human femur. We produced less than 100 nm thick electron transparent cross-sections of otherwise untreated bone. In accordance to previous work on collagen orientation patterns identified in demineralized specimens from the same bone samples we found a plywood type of stacking of mineral bundles with approximately one micrometer layer thickness [3]. On the nanoscale we identified different motifs of mineral orientation patterns labeled as ‘ordered’ and ‘lacy’. When studying those samples by electron tomography we find that the two motifs are not related to different pathways of mineral organization but to a well defined pattern of collagen orientation. This orientation changes by approx. 50-60° with an approx. micrometer periodicity giving rise to the generally observed ring pattern around the Haversian canals.


CRYSTALLIZATION MODIFIES THE STRESS-STRAIN BEHAVIOR OF COLLAGEN FIBERS

Invited
Collagen is the principal load-bearing protein in both mineralized and unmineralized mammalian tissues. In tendon, where collagen is usually unmineralized, an interface is formed with the solvent (most commonly water, but other organic liquids are also considered in this study) which significantly alters its tensile modulus. In bone, an organic-inorganic interface may also form via the crystallization of the hydroxyapatite mineral phase, which can result in an enormous increase in tensile modulus and stability. For example, the collagen in fossilized bone can resist degradation for periods up to 1 million years. In this work, we present strain-realistic molecular dynamics simulations combined with thermodynamic integration to investigate the interfacial energy of collagen systems. Direct scaling of the interfacial energy reveals the importance of solvent-induced surface stress, which stabilizes the triple helix structure via a circumferential (not radial) contraction. Results are corroborated by small- and wide-angle X-ray scattering experiments, and the confining effect of solvent is attributed mainly to the entropy change of solvent ordering around the triple helix. Using principal component analysis (PCA), we present Raman spectroscopy evidence for a mineralization-induced peak shift as a function of applied tensile strain. In particular, density functional calculations demonstrate that a collagen peak shift in the vicinity of 855 cm\(^{-1}\) results from changes in the pucker preference of proline rings. Finally, we demonstrate the connection between this proline ring pucker preference and stress transfer within the mineralized collagen structure.
ANALYSIS OF THE EFFECTS OF A ROTATING MAGNETIC FIELD ON THE GROWTH OF CADMIUM ZINC TELLURIDE BY THE TRAVELING HEATER METHOD
Zaoyang Li, Jeff H. Peterson, Andrew Yeckel, Jeffrey J. Derby
University of Minnesota, Minneapolis, MN

Large, single crystals of cadmium zinc telluride (CZT) are needed for portable, low-cost, and sensitive devices to detect radioactive materials. However, CZT is a particularly difficult material to grow, and advances in growth methods are needed. While the traveling heater method (THM) has been used to grow good-quality CZT, it is limited by growth rates several orders of magnitude smaller than competing melt growth processes. If constitutional supercooling effects are responsible for limiting growth in THM, the application of an external magnetic field may provide a means to promote melt mixing, ameliorate this instability, and promote faster growth. Rotating magnetic fields (RMF) have been successfully applied to many semiconductor melt growth systems to promote melt convection. The application of RMF produces Lorentz forces through the molten phase, and these forces can be tuned to profoundly impact melt flows. In turn, these flows modify heat and mass transfer, influencing segregation along and stability of the melt-solid interface. In addition, since the applied RMF can be instantaneously changed, it provides for a potentially ideal control action, if its complicated effects can be predicted and understood. In this presentation, we employ fundamental mathematical models solved via finite element methods to assess the impact of RMF applied to THM growth of CZT. The RMF applied externally to the melt can be expressed as a constant magnetic field rotating with a frequency $\omega$. The skin effect is ignored, as the electrical conductivity of CZT melt is relatively small and the frequency $\omega$ is usually not high. A leading-order model is used to calculate the induction electric potential field, and thus to take into consideration all the components of the Lorentz force. Adding the RMF significantly changes the melt convection pattern and promotes a more convex interface, as observed under microgravity conditions. Under terrestrial gravity levels, thermal buoyancy convection is strong enough to overcome the RMF flows and produce concave interface shapes. However, the additional flows driven by RMF can significantly influence the mass transport in the melt and affect compositional uniformity along the interface. This work has been supported in part by the National Science Foundation, under DMR-1007885, and no official endorsement should be inferred. Dr. Li has been supported by a China Scholarship Council Fellowship.

GROWTH AND CHARACTERIZATION OF BRIDGMAN GROWN DETECTOR GRADE CdZnTe BULK CRYSTALS IN PBN CRUCIBLE
Santosh K. Swain, Jedidiah McCoy, Rohan Rao, Kelvin Lynn
Washington State University, Pullman, WA

CdTe and its alloy CdZnTe have long been considered excellent materials for a wide range of radiation sensing applications. CdZnTe with 10 at% Zn is suitable for a high-resolution room temperature x-ray and gamma ray spectrometer because of its optimized band gap, average atomic number, high density etc. CdZnTe with 4 at% Zn is an excellent lattice-matched substrate choice for epitaxial growth of a HgCdTe infrared sensor. However, for most of these applications, high single crystal yield with uniform electro-optical behavior is desired. The Travelling Heater Method (THM) is currently the most successful commercial growth method. Although THM can produce large single crystal boules with excellent detector resolution, the performance to cost ratio is still an issue primarily because of the relatively long growth process and the requirement of post growth processing to eliminate flux inclusions. The Vertical Bridgman technique has been successful in obtaining high quality detector grade CdZnTe at a much faster production rate compared to THM. However, it suffers from issues such as poly-crystallinity, inhomogeneous Zn, and dopant distribution. This article presents implementation of a pyrolytic boron nitride (pBN) crucible to mitigate these challenges. CdZnTe bulk crystals have been grown using a pBN crucible for improved single crystal yield. Large single grain wafers have been obtained from the boules suggesting a pBN crucible provides a better method to avoid melt crucible interaction. This interaction has been a significant challenge in the melt growth of CZT. The detectors fabricated from the crystals exhibit high bulk resistivity ($>10^{6}$ ohm.cm) and $\mu$e values $>1$ x $10^{4}$ cm²/v. Room temperature photoluminescence measurement along the axial direction of the boule indicates nearly uniform Zn distribution which is usually difficult to achieve in melt growth. Eversion etching was performed on (111) oriented wafers which results in an etch pit density of $>4$ x $10^{4}$ cm². This work is supported by the Department of Energy, National Nuclear Security Administration, under Award DE-NA0002565, Dr. David Beach, Program Manager.
Thus, Nu for mass transfer (i.e. Sherwood number) is a function of the Grashof (Gr), Prandtl (Pr) and Schmidt (Sc) numbers. Because of the complexity of the natural convection in liquid metals, all correlations giving Nusselt numbers are empirical, based on laboratory experiments. Here, we derive a correlation for the effective segregation coefficient, $k_{eff}$, as a function of the equilibrium segregation coefficient ($k_0$), growth rate specified by the Peclet number, (Pe) and Nu. Thus, $k_{eff} = f(k_0, Pe, Nu)$ or $k_{eff} = f(k_0, Pe, Gr, Pr, Sc)$. The correlations are applied to the experimental and numerical data for Bridgman growth, conducted on earth and in microgravity and zone refining. Solid agreement is demonstrated.

2:15 PM - 2:30 PM
CZOCHRALSİ GROWTH OF LEAD IODIDE
Arne Croell1, Justus Tonn1, Andreas Danilewsky1, Marie Matuchova2
1University of Freiburg, Freiburg, Germany; 2Institute of Chemical Technology, Prague, Czech Republic

Lead iodide is a promising gamma-ray detector material due to its high Z number of 62.7 and a bandgap of 2.32 eV. Bulk crystals of PbI2 are usually grown by the Bridgman method. Typical problems include: a) the strong anisotropy in thermal conductivity due to the layered structure, leading to a thermocapillary orientation of the self-seeded crystals, with the c-axis tilted with respect to the ampoule axis and subsequent stress and crack formation of the crystals during cool down and b) the occurrence of oxidic impurities leading to partial sticking of the crystal to the ampoule wall and a degradation of the electrical properties. A hydrogen treatment of lead iodide was shown to be able to effectively reduce the oxidic impurities contained in the source material. Through thermal analysis (DTA, DSC/TG) of contaminated PbI2 the influence of the H2 treatment on the resulting material purity could be proven. At the same time, a hygroscopic nature of PbI2 could be disproved, and new results on the thermal behaviour and phase diagram of oxide-polluted PbI2 will be presented. The effectiveness of the H2 treatment is confirmed by single crystal growth experiments using the Czochralski technique. PbI2 crystals with improved structural properties compared to Bridgman growth and a reproducible crystallographic orientation through the preparation of oriented seeds could be achieved. Control problems due to (congruent) sublimation of PbI2 from the melt onto the cold parts of the furnace including the observation window could be overcome by modifying the gas flow in the chamber and changing the feedthroughs. Quantitative data on the anisotropy of the thermal conductivity will also be presented.

2:30 PM - 2:45 PM
DEVELOPMENT OF THE CZOCHRALSKI TECHNIQUE FOR SINGLE CRYSTAL GROWTH OF MIXED ALKALI EARTH HALIDES
Didier Perrodin, Zewu YAN, Ivan Khodyuk, Gregory Bizarri, Edith Bourret
Lawrence Berkeley National Laboratory, Berkeley, CA

Development of the Czochralski Technique for Single Crystal Growth of Mixed Alkali Earth Halides
D. Perrodin, Z. Yan, I. Khodyuk, G. A. Bizarri, E. D. Bourret
Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Barium halides (BaX2, X= F, Cl, Br, I) form solid solutions that have been studied in the last years due to their propensity to be excellent scintillators when activated by Eu2+. For future commercialization they are also attractive as it is anticipated that the cost and availability of the raw materials will allow for production of affordable crystals, a requirement for large-scale deployment. The main impediment to their large-scale production is the low crystal growth yield and reproducibility of the growth technique. Up to now, they have been synthetized in polycrystalline forms and as small size single crystals by the vertical Bridgman-Stockbarger technique. Here, we report on the development of the Czochralski growth of 1 to 1.5" in diameter crystals of the ternary: BaBrI2 activated with Eu2+. The liquidus solidus separation of the BaBrI2 solid solution is very small allowing growth of crystal with uniform composition as demonstrated by the measured scintillation performance. We have recorded energy resolutions of 3.6% homogeneously distributed along bulk single crystals and an average of 60,000 ph/MeV light output. These values are still below what is expected from that material [1] but we find that the Czochralski process, a commercially viable production tool with high yield, can be used and further developed for growth of the mixed halides. BaBrCl2:Eu2+ was also produced successfully by this technique. We will present various aspects of the growth process: the subtle seeding, stoichiometry control, melt cleaning procedure and growth parameters.


BaBrCl2 Czochralski seed BaBrCl2 single crystal

This work was supported by the US Department of Homeland Security/DNDO and carried out at Lawrence Berkeley National Laboratory under Contract no. AC02-05CH11231. This work does not constitute an express or implied endorsement on the part of the government.
Thursday, August 6, 2015
1:30 PM - 3:00 PM

Industrial Crystal Growth Technologies and Equipment (ACCGE) 3

Location: Madison
Session Chair(s): Matt Whittaker

1:30 PM - 2:00 PM
GROWTH OF FARADAY ROTATOR MATERIALS FOR OPTICAL ISOLATOR APPLICATIONS
Invited
Kevin T. Stevens¹, Greg Foundos¹, John Sundeen¹, Allen Brady¹, David E. Zelmon², Emily C. Erdman²
¹Northrop Grumman SYNOPTICS, Charlotte, NC; ²Air Force Research Lab, Dayton, OH

Northrop Grumman SYNOPTICS is a leading supplier of single-crystal laser materials grown by the Czochralski technique. In addition to laser-gain materials, SYNOPTICS grows and supplies terbium gallium garnet (TGG) crystals for optical isolator applications. With the recent advancements in fiber lasers, Faraday materials have become increasingly important to combat optical feedback by means of optical isolation.

In order to meet the demand of increasing output powers of fiber lasers, improvements are needed in Faraday materials. In particular, larger apertures, lower absorbing materials, and improved intrinsic material properties are required. Improvements in the growth of single crystal TGG will be presented. Processes that provide consistently low absorption and large aperture crystals will be discussed. In addition, new materials with low nonlinear refractive indices are needed to handle higher output powers. Two fluoride crystals, terbium lithium fluoride (TLF) and potassium terbium fluoride (KTF), exhibit promising characteristics. Growth and characterization of these two crystals will be presented.

2:00 PM - 3:00 PM
LASER HEATED PEDESTAL GROWTH OF YB DOPED CAALGDO4
Invited
Gisele Maxwell, Bennett Ponting, Emetet Gebremichael, Ruben Magana
Shasta Crystals Inc., san francisco, CA

Yb doped CaAlGdO4 (Yb:CALGO) is a very promising material for the development of diode-pumped femtosecond lasers, both for its broad emission band, and very good thermal conductivity properties. This works presents the growth of Yb:CaAlGdO4 by laser heated pedestal growth, to our knowledge for the first time. Crystals with diameters between 25 μm and 1mm were successfully grown. We will discuss how growth parameters and synthesis processes used to make the feed rods influence the quality and performance of the Yb:CALGO crystals.

2:30 PM - 3:00 PM
STRATEGIES FOR IMPROVING INDUSTRIAL CRYSTAL GROWTH PROCESSES
Hunter Marshall
CTG Advanced Materials, Bolingbrook, IL

There are controllable parameters fundamental, and frequently common, to all industrial crystal growth processes. To optimize the output of an industrial crystal growth process there are preferred, but sometimes not obvious, strategies for understanding and successfully controlling the critical crystal growth parameters.
In-situ x-ray scattering is a powerful tool to investigate the mechanisms of crystal and epitaxial film growth at an atomic scale [1,2]. With the advent of coherent x-ray techniques that take advantage of continuing increases in x-ray source brightness [3], we are developing a next-generation instrument for in-situ synchrotron x-ray studies of crystal growth that has the high accuracy and stability required for studies with coherent x-ray beams. The instrument will implement advanced x-ray techniques, including coherent diffraction imaging, x-ray photon correlation spectroscopy (XPCS), and nanodiffraction, to open a new window onto atomic dynamics during growth. For example, the dynamics of atomic steps and islands revealed by XPCS will shed new light on epitaxial growth mechanisms.

The six-circle diffractometer system includes a two-dimensional x-ray detector and long detector arm with the stability needed for coherent x-ray studies. The sample goniometer incorporates a large hexapod to precisely support and position a variety of chambers for different materials and processes. The system will include the first of a new generation of chambers, designed for OMVPE experiments with samples heated to 1500K in chemically active precursor flows, maintaining sub-micron positional stability and full rotation. It is provided with systems to safely and accurately control and monitor hazardous gases. The flexible platform supports chambers incorporating ports for grazing-exit fluorescence and optical spectroscopy for characterization of surface composition and chemistry during growth. In this talk we will present initial results characterizing this system for studies of OMVPE growth of GaN-based materials.


OMVPE system with x-ray diffractometer for in-situ nitride materials synthesis studies. The instrument is located at the Advanced Photon Source beamline12ID-D.

1:50 PM - 2:10 PM
IN-SITU OPTICAL MONITORING OF QUANTUM CASCADE LASER STRUCTURES DURING MOVPE GROWTH
Andrey Krysa, John Roberts, Dmitry Revin, John Cockburn
University of Sheffield, Sheffield, United Kingdom

In this paper we summarize our experience with in-situ optical monitoring during epitaxy of InGaAs/InAlAs on InP and GaAs/AlGaAs on GaAs heterostructures for quantum cascade lasers (QCLs). We demonstrate the effectiveness of this technique to monitor the epitaxial process and manufacturing of QCL devices.

Developing an epitaxial process for QCLs is a challenging task from many points of view. Firstly, the active regions of QCLs comprise of hundreds (or even thousands) quantum wells and barriers which are just a few atomic monolayers thick. QCL performance critically depends on the precision of these layers, with respect to thickness, composition and interface abruptness. Secondly, a complete assessment and quality control of QCL epi-wafers has never been straightforward and conventional assessment takes a relatively long time. Therefore, the structural information provided by in-situ optical monitoring is crucial for a successful QCL epitaxial process.

MOVPE was performed using an AIXTRON 7×2" (or 3×3") close coupled showerhead reactor equipped with a LayTec EpiTT in-situ 950 nm and 633 nm optical monitoring system. The susceptor rotation speed was set at 100 rpm or 200 rpm. The growth rates of the claddings and core region materials (i.e. InP, InGaAs, InAlAs etc) were derived from the EpiTT data following calibration growth runs. This data was in a good agreement with X-ray diffraction measurements. However, the latter technique required additional growth runs of dedicated superlattices (e.g. InGaAs/InAlAs).

EpiTT surface reflectance recorded from a complete InGaAs/InAlAs/InP QCL growth allows identification of all the constituent layers of the structure. The number of the reflectance oscillations seen within the gain region corresponds to the number of cascade stages. We also observed a fine structure within one oscillation period which can be unambiguously associated with the growth of particular InAlAs and InGaAs layers within one cascade stage. Similar features in the reflectance spectrum were observed during growth of GaAs/AlGaAs QCLs with AlInP (or GaInP) claddings. The shorter wavelength light probe and higher susceptor rotation speed resulted in a better resolution of the thin (~ 1 nm) layers in the gain region.

We have also collected many examples of various failures such as wafer bowing caused by lattice mismatched compositions, fluctuations of reagents delivery and epitaxial surface roughening which were observed by optical monitoring during QCL epitaxy.

2:10 PM - 2:30 PM
LARGE AREA SEMI-POLAR (11-22)-GAN: HETEROEPITAXIAL GROWTH OPTIMIZATION WITH THE AID OF IN-SITU METROLOGY
Frank Brunner, Markus Weyers
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Non- and semi-polar nitride-based LEDs are under ongoing investigation due to the reduction of polarization effects which can improve the device performance. However, free-standing semi-polar GaN substrates are still small in diameter (< 1 inch) and expensive. Therefore, hetero-epitaxially grown semi-polar layers continue to be of interest due to the much lower cost and larger wafer sizes available. In this work, we use 100 mm diameter r-plane sapphire substrates patterned with trenches (r-PSS) exhibiting c-plane-oriented sidewalls. Selective growth by MOVPE of GaN in c-direction results in coalescence of the semi-polar (11-22) surface featuring a reduced defect density.

Epitaxial growth is optimized with the aid of in-situ monitoring to trace GaN coalescence behavior, surface morphology and wafer bow (Fig. 1). Wafer pocket temperature is measured pyrometrically on a planar sister wafer since the low-reflecting PSS hinders a proper emissivity correction. Reflectance measurements enable coalescence speed and growth rate determination and give fingerprints of the final layer morphology. Especially, size and density of typical semi-polar GaN surface defects can be controlled by near-UV reflectance measurements. Concave wafer curvature at growth temperature exceeds typical values of c-oriented GaN, whereas the convex bow at room temperature is spherical and comparable to polar material. In-situ bow analysis implies that the thermal expansion mismatch between (11-22)-GaN and r-PSS increases significantly at temperatures above 1000°C.
IN SITU MEASUREMENT OF BULK III-V ATOMIC ORDERING USING TWO-DIMENSIONAL WAFER CURVATURE

Ryan M. France, William E. McMahon, Joongoo Kang, Myles A. Steiner, John F. Geisz
NREL, Golden, CO

Atomic ordering of III-V ternaries and quaternaries is known to affect the optical and electrical properties of the alloy. The influence of ordering on the structural and mechanical properties is less often considered. Bulk CuPt ordered alloys can be elongated along the normal to the (111) ordered planes, resulting in a rhombohedral distortion. When epitaxial on a (001) cubic substrate, ordered III-Vs have an asymmetric strain with a maximum between the two in-plane <110> directions. Here, we demonstrate in situ measurement of the anisotropic strain due to ordering using two-dimensional wafer curvature. The measurement is sensitive to bulk anisotropies, and so is complementary to other in situ measurements that are sensitive to surface anisotropies. Using ab initio calculations, we determine a maximum strain anisotropy of 0.27% between [110] and [1-10] when perfectly ordered single-variant GaInP2 is coherent to a (001) cubic substrate (Fig. 1a). In practice, the ordering is never perfect, but a measureable strain anisotropy exists (Fig. 1b). We relate the in situ measurement of strain anisotropy on various GaInP2 samples to ex situ measurements (XRD, PL) of the order parameter to validate the measurement and confirm the capability to predict material properties. We show the utility of this technique for quickly determining the effect of growth conditions and surfactants on ordering in lattice-matched GaInP and GaInAs. More generally, this measurement technique could in principle be used to monitor phase...
changes in any epitaxial system for which the strain anisotropy of the two phases differs.

Fig. 1 (a) Illustration of the strain anisotropy, $\Delta \varepsilon$, resulting from pseudomorphic epitaxy of rhombohedral ordered III-V materials on cubic (001) substrates. (b) 2D curvature and strain anisotropy throughout 3 $\mu$m of GaInP2 growth with Sb surfactant turned on and off periodically to vary the order parameter. Layers with and without Sb flow are demarcated by the vertical lines, and clear changes in the 2D curvature and strain anisotropy are observed.
and remineralized using a PILP process (pH=7.4, 14 days) with CaP solution containing poly(ASP) (27 KDa). De
proteins. Method: Artificial carious lesions with lesion depths of 140 µm were cr

“polymer

Objective: Preservation and reinforcement of demineralized carious dentin or inherited dentin defects caused by mutations in
the dentin sialophosphoprotein (DSPP) gene with an effective re-mineralization treatment is of paramount importance. In this study, we
used an artificial carious human dentin and/or Dspp knockout (Dspp−/−) mouse model that displays a phenotype similar to human
dentinogenesis imperfecta type II (DGI-II), to test the hypothesis that poly-L-aspartic acid [poly(ASP)] as used for so-called
“polymer-induced liquid-precursor” (PILP) mineralization may restore its mechanical properties, a critical role attributed to DSPP
proteins. Method: Artificial carious lesions with lesion depths of 140 µm were created with 0.05 M acetic acid (pH=5.0, 66 hours),
and remineralized using a PILP process (pH=7.4, 14 days) with CaP solution containing poly(ASP) (27 KDa). De- and remineralizing
procedures were performed in the presence or absence of matrix metalloproteinases (MMP)-inhibitors. This inhibitor was included to prevent digestion of the collagen fibrils. For Dspp knockout simulating DGI-II, mandibular first molars of six-week old Dspp−/− and wild-type mice were isolated, resin embedded and sectioned. Cross-sections from Dspp−/− dentin were treated with the PILP system. Mechanical recovery of demineralized dentin and Dspp−/− dentin following PILP mineralization were examined and measured in water with nanoindentation. Result: In the presence of MMP-inhibitors, the hydrated artificial lesions recovered elastic moduli in the outer, more demineralized zone to levels of 80%. The improved mechanical response was attributed to preservation of collagen integrity by protease inhibitors. In the absence of inhibitors mechanical recovery was delayed and not as elevated. For inherited dentin defects; PILP-treatments of dentin from Dspp−/− mice successfully restored its properties and structure of the tissue, suggesting that poly(ASP) may act in a similar fashion as DSPP proteins to guide tissue remineralization. In conclusion, this proof-of-concept biomimetic remineralization approach can open new approaches towards an in situ strategy for hard tissue repair and engineering.

This work was supported by NIH Grants 2R01 DE016849 and CTSI-SOS Grant Award # 000166.

2:45 PM - 3:00 PM
Biomimetic Randall's Plaque as an In Vitro Model System for Studying the Role of Acidic Biopolymers in Idiopathic Stone Formation
Archana Lovett, Douglas Rodriguez, Saeed Khan, Laurie Gower
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Randall's plaque (RP) deposits seem to be consistent among the most common type of kidney stone formers, idiopathic calcium oxalate stone formers. This group forms calcium oxalate renal stones without any systemic symptoms, which contributes to the difficulty of understanding and treating this painful and recurring disease. Thus, the development of an in vitro model system to study idiopathic nephrolithiasis, beginning with RP pathogenesis, can help in identifying how plaques and subsequently stones form. One main theory of RP formation is that calcium phosphate deposits initially form in the basement membrane of the thin loops of Henle, which then fuse and spread into the interstitial tissue, and ultimately make their way across the urothelium, where upon exposure to the urine, the mineralized tissue serves as a nidus for overgrowth with calcium oxalate into a stone. Our group has found that many of the unusual morphologies found in RP and stones, such as concentrically laminated spherulites and mineralized collagenous tissue, can be reproduced in vitro using a polymer-induced liquid precursor (PILP) process, in which acidic polypeptides induce a liquid phase amorphous precursor to the mineral, yielding non-equilibrium crystal morphologies. Given that there are many acidic proteins and polysaccharides present in the renal tissue and urine, we have put forth the hypothesis that the PILP system may be involved in urolithiasis. Therefore, our goal is to develop an in vitro model system of these two stages of composite stone formation to study the role that various acidic macromolecules may play. In this current study, the development of “biomimetic” RP is investigated, which will then serve as a nidus for calcium oxalate overgrowth studies. Decellularized kidney tissue is used as it a model scaffold of the native tissue in which plaque forms because it contains many renal tubules with their basement membranes, as well as interstitial tissue, providing a rather realistic model substrate. The papilla regions are mineralized and then characterized to determine if the morphologies match that of native plaque. The ultimate goal is to develop strategies to avoid RP and its detrimental consequences in stone formation, or developing therapeutic treatments to prevent or cure the disease.
Strontium titanate (SrTiO₃) is one of the most commonly used substrate materials for the epitaxy of perovskite thin films. However, advanced applications are limited by the high dislocation density (> 10⁵/cm²) of the currently commercially available crystals which are grown by the Verneuil method. Only few crystal growth methods are suitable to meet the demands for high-quality, large crystals. Among them crystal growth by the optical floating zone method was the favoured method so far. It can be used to reduce the dislocation density by more than one order of magnitude to (1-5) x 10⁴ cm⁻² for bulk crystals (15-20 mm in diameter) [1]. Recently we have shown that high quality bulk crystals (25 – 29 mm in diameter) can be grown by top-seeded solution growth from self-flux [2]. Typical etch pit densities are in the range between 2 x 10² and 2 x 10⁴ cm⁻². To overcome the disadvantage of low growth rates typically for solution growth, we demonstrate that bulk SrTiO₃ single crystals of good perfection can also be grown from a stoichiometric melt. One of the relevant methods is the edge-defined film-fed (EFG) growth which allows rather high growth rates. However, this method as well as the most desirable Czochralski method (as the highest developed growth technology for bulk crystals of high perfection) suffer hitherto from growth instabilities. Additionally, Czochralski growth also suffers from spiral formation and subsequent spiraling. In spite of these early difficulties we realized the growth of high quality bulk crystals from the melt by using the EFG method. Straight cylindrical crystals with diameters of 15 mm and lengths of up to 60 mm were grown. Also disc-shaped crystals with diameters up to 2 inch were grown by the Czochralski method but for large diameter crystals the maximum possible crystal length is usually limited to 15 mm under our conditions.


Piezoelectric single crystals are nowadays essential for a wide range of application (filter, resonator, sensor⋯). Despite the market is led by very well-known materials (Quartz, LN, LT), the needed for higher quality, better coupling and higher thermal stability encourage the development of new materials to enlarge the applications based on electro-mechanical conversion. To reach this goal, one of the most promising material family was determined to be Langasite crystals which were developed for several decades. Belonging to this family, LGT (La₃Ga₅.5Ta0.5O₁₄) was established to be the best member in term of coupling factor or quality factor (Qf).

In this study, we propose to present the growth of large La₃Ga₅.5Ta0.5O₁₄ (LGT) crystals by the Czochralski technique along (001) (Z), and 100 (X) directions. To obtain high quality performed crystals, starting composition, and thermal setting and growth conditions (pulling rate, rotation, atmosphere) were investigated to grow crystal under stationary stable regime without any macroscopic and microscopic defects. Through those improvements we succeeded to grow large bulky crystal free of cracks and defects. The grown crystals were characterized by different techniques, including structural (Raman spectroscopy, X ray diffraction) and optical measurements (Absorption, IRFT.) to confirm their high quality.
present. It is certainly true that the color center is caused by the oxygen defect that happens when the crystal is grown or thermally treated in reduced atmosphere. However, such an oxygen deficiency is as small as the order of ppm and not considered here. The variation of oxygen, here, is comparable to the charge compensation due to the impurity or to the segregation during growth and its amount may be up to the order of mol%.

We here consider two issues. First the oxygen is normally insufficient or exceeded in the diffusion boundary layer, which means that the oxygen-metal stoichiometric relationship does not hold in the liquid near the interface. This has not been well appreciated for many years, but it is proved by a simple experiment. The crystallization electromotive force (c-EMF) arises during growth since the segregation of ionic species in the melt near the interface yields a net charge of one sign whereas the opposite sign in the solid across the interface. The presence of such a non-zero potential suggests the invalidity of the stoichiometric relationship between metal and oxygen in the melt near the interface. However, once the melt containing insufficient or excess oxygen crystallizes, it crystallizes in such a way that the metal-oxygen stoichiometry is held since the stoichiometric relationship is necessary in order to determine the population of each of solid species.

4:30 PM - 4:45 PM
BULK SINGLE CRYSTALS AND PROPERTIES OF TRANSPARENT SEMICONDUCTING OXIDES: \(\beta\)Ga2O3, In2O3, SNO2 and MgGa2O4

Zbigniew Galazka, Reinhard Uecker, Klaus Irmscher, Detlef Klimm, Mike Pietsch, Martin Albrecht, Albert Kwasniewski, Martin Naumann, Robert Schewski, Matthias Bickermann
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\(\beta\)Ga2O3, In2O3, SnO2 and MgGa2O4 are attractive transparent semiconducting oxides (TSOs) with wide bandgaps of 4.8, 2.8, 3.5-3.8, and 4.9 eV, respectively. They are, however, chemically unstable at elevated temperatures and tend to decompose, therefore growing such single crystals from the melt is a very challenging task. 2-inch diameter \(\beta\)Ga2O3 single crystals (melting point, \(\text{MP}=2000°C\)) were grown from the melt by the Czochralski method; over 1-inch diameter In2O3 single crystals (\(\text{MP}=1950°C\)) - from the melt with use of our novel crystal growth technique under the name Levitation-Assisted Self-Seeding Crystal Growth Method (LASSCGM), while 1-inch diameter SnO2 single crystals (\(\text{MP}>2100°C\)) - from the gas phase by the physical vapor transport (PVT), since melt growth of SnO2 is rather not possible. Additionally, we have discovered a semiconducting behavior of MgGa2O4 under certain growth conditions. MgGa2O4 is the most stable compound as compared with other TSOs and was grown from the melt (\(\text{MP}=1930°C\)) with use of different techniques. This report will focus on basic aspects of crystal growth, crystal quality and electrical / optical properties of both as-grown and annealed crystals. An extensive characterization of the crystals showed that their structural quality is fully compatible with their use as substrates for epitaxial deposition. Availability of bulk TSO single crystals combined with their unique properties offers opportunities for developing novel devices for high power electronics, transparent electronics, lighting, and gas sensing.

4:45 PM - 5:00 PM
CA3NBGa3Si2O14 PIEZOELECTRIC FIBER CRYSTAL FOR ELECTRICAL GENERATION FROM OSCILLATION GROWN BY MICRO-PULLING-DOWN METHOD

Masanori Kitahara, Yuui Yokota, Yuji Ohashi, Andrey Medvedev, Syunsuke Kurosawa, Kei Kamada, Osamu Eguchi, Akira Yoshikawa

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Langasite-type single crystals with A3BC3D2O14 chemical composition (point group: 32 space group: P321) have been investigated as a piezoelectric material for some applications of piezoelectric sensor at high temperature and small-size oscillator with low power consumption due to the high electromechanical coupling factor and high temperature stability of frequency. In 1900s, La3Ta0.5Ga5.5SiO14 (LTG), La3Ga5SiO14 (LGS) and La3Nb0.5Si5.5O14 (LNG) single crystals with a disordered structure have attracted attentions due to their high piezoelectric constant and electromechanical coupling factor in a wide temperature range. In addition, novel langasite-type crystals with an ordered structure as represented by Ca3NbGa3Si2O14 (CNGS), Ca3TaGa3Si2O14 (CTGS), Sr3NbGa3Si2O14 (SNGS), and Sr3TaGa3Si2O14 (STGS) have been developed in 2000s and their piezoelectric properties were investigated in detail. The langasite-type crystals with the ordered structure have higher electrical resistivity in high temperature and lower crystal impedance than the crystals with the ordered structure.

Some constructions such as building and bridge have each intrinsic oscillation and most of the oscillation energies are not used. Therefore, we are developing piezoelectric crystals which can generate electrical power by the intrinsic oscillations of constructions. We have designed the configuration of the piezoelectric element and we tried to grow the langasite-type fiber crystal with high aspect ratio according to the oscillation value of the buildings and bridge in this study. We grew CNGS fiber crystal with high aspect ratio by a micro-pulling-down (\(\mu\)-PD) method which could grow a fiber crystal directly and control the shape of grown crystal. Starting materials, CaCO3, Nb2O5, \(\beta\)Ga2O3, SiO2 (>4N purity), were mixed as the nominal composition of Ca3NbGa3Si2O14 and the mixed powder was sintered. The sintered powder was entered in a Pt crucible with a die at the bottom. The crucible was heated up to the melting point of CNGS and the fiber crystal was grown using CNGS seed crystal. By the crystal growth, CNGS fiber crystal with high aspect ratio could be grown and shape of the grown crystal could be controlled by the die of the crucible. Crystal state and physical properties of the grown fiber crystal were evaluated as the piezoelectric element. The detail of crystal growth and the results of evaluations will be reported.
study, 3 inch size single crystals of Ce:GAGG was successfully grown. The detailed results on chemical analysis, light yield, about ~90 ns at emission around 520 nm, prospective light yield of about 46000 photon/MeV, and density of 6.6 elements. Recently, our group reported about Ce

Scintillators play important role in many fields such as high-energy physics, medical imaging, geological exploration and homeland security. Oxide materials based on garnet structure single crystals are promising candidates for scintillator applications, because of well mastered technology developed for laser hosts and other applications, optical transparency and easy doping by rare-earth elements. Currently, our group reported about Ce-doped Gd3Ga3Al2O12 (Ce:GAGG) single crystal and scintillation response of about ~90 ns at emission around 520 nm, prospective light yield of about 46000 photon/MeV, and density of 6.6 g/cm3. In this study, 3 inch size single crystals of Ce:GAGG was successfully grown. The detailed results on chemical analysis, light yield, decay
time and timing resolution will be reported.

Stoichiometric mixtures of 4N CeO2, Gd2O3, β-Ga2O3 and α-Al2O3 powders were used as starting material. Ce1%:GAGG single crystals were grown by means of the Cz method using an RF heating system. The rotation rate was 1-10 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. Crystals were grown from a 150 mm diameter Ir crucible under N2 with adding 30% of CO2 atmosphere to prevent evaporation of gallium oxide. The seed crystal was a [100] oriented Ce:GAGG crystal. To determine the light yield, we obtained the pulse height spectra of these crystals irradiated with gamma rays from a 137Cs (662 keV) source. Scintillation photons were detected with a photomultiplier tube (APD, S8664-55 Hamamatsu). The signals were amplified with a preamplifier, shaped with a shaping time of 2 μsec and read out with a multi-channel analyzer.

Growth conditions such as con angle, rotation rate, and heat insulation design in the furnace were optimized for obtaining crack-free 76mm diameter and 100mm length Ce:GAGG crystals with uniform light yield in whole crystal. The solidification yield of grown crystal was about 25% of the melt of raw material in the crucible. The light yield of Ce:GAGG with 5 x 5 x 5 mm size was around 56000 photon/MeV. The energy resolution was 5.2%@662keV. The relationship between charge of chemical composition and scintillation properties on solidification fraction (g) will be reported. Furthermore, result of timing resolution measurements will be also reported.

4:45 PM - 5:00 PM

THERMOELECTRIC POWER GENERATION USING SILICIDES AND LEAD MAGNESIUM TELLURIDE

Patrick Taylor1, Sudhir Trivedi1, Susan Kutcher1, Wiltod Palosz1, Dajie Zhang1, Jogender Singh1, Narasimha Prasad1
1U.S. Army Research Laboratory, Adelphi, MD, 2Brimrose Technology, Sparks, MD, 3Pennsylvania State University, University Park, PA, 4NASA Langley Research Center, Hampton, VA

Thermoelectric Power Generation (TEPG) is the most efficient and commercially deployable power generation technology for harvesting wasted heat. A thermoelectric power generator is a solid state device that directly converts heat into electricity, and offers several distinct advantages over other technologies. Despite these advantages, practical use of TEPG has been impeded because the energy conversion efficiency of today’s state-of-the-art TE generators is significantly lower than that of conventional power generators. This paper will present the development of two novel TEPG materials: bulk nano-composites of magnesium silicide (Mg2Si) / manganese silicide (MnSi) and bulk nano-composites of lead magnesium telluride (PbMgTe). Compared with other thermoelectric materials operating in the same temperature range, Mg2Si and MnSi are environmentally friendly, have constituent elements that are abundant in the earth’s crust, non-toxic, lighter and cheaper. We have previously successfully produced a device from Mg2Si and MnSi material with good TE properties (Seebeck coefficient of roughly 120 mV/K on average per leg). Our results indicate that we are on track to develop materials with ZT on the order of 1.6 or higher. PbTe based materials have been found to have exceptional base thermoelectric performance in the intermediate temperature range of 400-1000K, and it has been found that alloying with MgTe can improve the performance even further. The bulk nano-composite materials are produced using the Field Assisted Sintering Technique (FAST) also called spark plasma sintering. FAST is an innovative process that sinters powder with 100% theoretical density. The short processing cycle leads to significant pay off in maintaining nanometer dimensionality as well as reducing the manufacturing cost of the components and the finished device. Material and device issues will be discussed including overall design, ohmic contact material and application procedures, and development of optimal thermal management material and techniques.
Thursday, August 6, 2015
3:30 PM - 5:00 PM

Nanocrystals, Quantum Dots and Nanowires (Joint ACCGE/OMVPE) 1

Location: Gallatin
Session Chair(s): Hoe Tan

3:30 PM - 4:00 PM

A TUNABLE LIBRARY OF CHALCOGENOUREA PRECURSORS TO COLLOIDAL QUANTUM DOTS: KINETICS AND MECHANISM OF NUCLEATION AND GROWTH

Invited
Jonathan Owen
Columbia University, New York, NY

We report a metal sulfide precursor platform based on inexpensive and air stable substituted-thioureas. Primary and secondary thioureas are prepared in multi-gram quantities under ambient conditions by mixing commercially available N-substituted isothiocyanates and primary or secondary amines. The substitution pattern tunes the precursor to monomer conversion kinetics over more than five orders of magnitude. Among a series of N-(p-X-C6H4)-N'-(n-dodecyl)-thioureas (X = OMe, Cl, H, CF3, CN) the rate of reaction with lead oleate increases 8x as the para-substituent varies from electron rich to electron poor. A linear relationship between the conversion rate and the concentration of PbS nanocrystals is observed across this series, allowing diameters from 2 - 8 nm to be prepared in quantitative yields. Using an automated high throughput synthesis platform, we have investigated the dependence of nucleation on the conversion rate and the conversion temperature. Using these results we identify conditions that lead to small PbS nanocrystals (d = 2.5 nm) with narrow size distributions in 10 gram quantities and at conversion rates that are not limited by the kinetics of mixing. The relationship between conversion kinetics, reaction temperature, and the final nanocrystal size and size distribution will be discussed.

4:00 PM - 4:20 PM

INFLUENCE OF CO SUBSTITUTION ON STRUCTURAL AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE BARIUM STRONTIUM HEXAFERRITE

Ezhil Vizhi R 1, Hankrishnan V 1, Saravanan P 2, Rajan Babu D 1
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Hexagonal ferrites of the M-type are of enormous technical importance in the permanent magnet industry because of their low price along with reasonable magnetic performances [1]. M-type structure (magnetoplumbite) which has the chemical formula of MFe12O19 (M=Ba, Sr, Pb) has enormous amount of peculiar features when compared with other structures. For example they have high Curie temperature, moderate saturation magnetization, excellent chemical stability and high corrosion resistivity [2]. They have wide range of uses in several applications like magnetic recording industry and microwave devices. In the present work, we have combined both Sr2+ and Ba2+ with the chemical formula of Ba0.5Sr0.5Fe12O19. We have again substituted Co2+ to the Fe3+ site and studied the structural and magnetic properties. We used solgel combustion process in order to synthesis the structure with the chemical formula Ba0.5Sr0.5Fe12-xCoxO19 (x=0.5, 0.7, 0.9) [3]. Here citric acid was used as the fuel. The synthesis consisted of a two-step process. Initially the structure was confirmed using XRD patterns. From the XRD patterns it was clear that as the doping level increased the intensity of (201) plane increased which showed that diffusion had occurred in the basic structure. We had studied the structure with the help of Fourier Transform Infrared Spectroscopy, we found that there was a shift in the octahedral and tetrahedral bands. There are 42 raman active bands according to the literature [4]. We have also reported the raman analysis of the synthesised samples. It showed 4 major raman active peaks for the M-type hexagonal structure. The Field emission scanning electron microscope and Energy dispersive X-Ray analysis was employed in order to study the morphology and composition of the nano crystalline Ba0.5Sr0.5Fe12-xCoxO19 (x=0, 0.5, 0.7, 0.9). The Transmission electron microscopy analysis was employed in order to analyse the distribution of particles and also to determine the particle sizes. The magnetic properties were analysed using the SQUID Magnetometer. The magnetic properties at room temperature were analysed and it showed a decrease in the coercivity as the doping level increased.
ELECTRON DIFFRACTION AND HIGH RESOLUTION TEM STUDY OF NOBLE METALS NANOCLEUSTERS ON TIN DIOXIDE NANOLAYERS SURFACE
This work meets the trends of fundamental and applied researches in the material sciences of semiconductors with sensor properties, which are capable to detect the presence of toxic and explosion-dangerous gases in air - gas mixtures [1]. For the first time by electron diffraction and HRTEM methods the SnO2 films surfaces modified by vacuum condensation of noble metals nanolayers with the subsequent thermal annealing in atmosphere of pure hydrogen were studied. The results of phase structure and substructure analysis have shown that after deposition Ag layers with thickness ~ 7 nm and ~ 20 nm on SnO2 surface the island substructure via Volmer-Weber mechanism is realized. After training in pure H2 atmosphere the flat Ag clusters with arbitrary orientation and with weak lateral faceting were formed. The sizes of Ag islands were 3 - 13 nm and 5 - 30 nm in a diameter for deposited nanolayers with thickness ~ 7 nm and ~ 20 nm respectively. The observed moiré patterns in Ag islands demonstrate that dislocations missed in them. The study of the morphology, the orientation, and the subpatterns of Au clusters on the surface of SnO2 films has shown that their formation process was similar as for Ag clusters. The diffraction contrast within the limits of separate islands of Au determines the presence of multiply twinned islands. The morphology of 3D Ag and Au clusters on SnO2 surface observed by TEM method is evidence of a weak metal - SnO2 interaction on interfacial boundary. The study of SnO2 films surface modified with Pd nanolayers has shown that the formation process of clusters Pd differs by some features as contrasted to Ag and Au. The Pd islands for coating thickness ~ 6 nm are characterized by an arbitrary distribution on SnO2 surface and have no crystallographic facetting. The increase of thickness of Pd coating up to ~ 40 nm results in formation of labyrinth substructure. It has been established that at the same thickness of initial metal nanolayers Pd clusters density is much higher than for Ag or Au clusters. This fact is explained by lower mobility of Pd adsorbed atoms. The design of the methods, which are able to modify SnO2 films surface by noble metals possessing catalytic activity, promotes the increase of sensors selectivity.

References

DESIGN OF INTERFACES IN CERAMIC/METALLIC MATERIALS FOR HIGH ENERGY ENVIRONMENTS
Hussein M. Zbib
Washington State University, Pullman, WA

Interfaces in metals, ceramics and alloys play a decisive role in determining the thermo-mechanical behavior under extreme loading and environmental conditions. To rationally design and accelerate discoveries of new material systems with novel thermo-mechanical properties-be it high temperature strength, corrosion resistance, fatigue life or any other mechanical property- the ability to predict the macroscopic properties on the basis of microstructure and interface structure is needed. The purpose of our work is to address this need by designing an engineered type of metal/ceramic nanocomposites with engineered nanolaminate structures that can exhibit very high strengths, fracture and fatigue resistance, thermal stability and corrosion resistance under high environment. Although refractory ceramic materials such as NbC and TiC, have high temperature strength and resistance to thermal shock and damage from thermal cycling, they are relatively brittle material with limited ductility and strength. However, laminate structures made of nanolayers with high density of incoherent interfaces (e.g. Nb on NbC and TiN on Ti), can have superior mechanical properties with strong resistance to thermal and environmental damage. The metal/ceramic composites can be created layer by layer by gas phase atomic layer deposition which is useful for high aspect ratio and large area system in short times. An electrochemistry deposition may be used as well for many combinations of composites and layer thickness and morphology by changing the growth temperature, with the aim of optimizing thermo-mechanical properties. In our work, we employ a novel computational material-by-design approach that includes a multiscale computational framework bridging molecular and dislocation dynamics (microscale) with crystal plasticity (mesoscale) to (a) design composites with nanolaminates that can serve as the fundamental basis for metal/ceramic systems, and (b) study the thermo-mechanical properties, deformation, fracture and fatigue and corrosion resistance of a number of possible combinations of these nanocomposites.
At the nanoscale, these ELRs self-assemble into 5 nm wide twisted filaments consisting of several β-spirals. These filaments are formed by purely inorganic processes, silica-carbonate biomorphs form life-like shapes such as carhart leaves and twisted helices. These structures consist of densely packed crystalline nanorods that co-align in a hierarchical assembly. We report the existence of an additional level of self-organization that creates oscillatory height variations in the biomorph sheets. The topographic features form concentric rings or disordered, patchy patterns that—based on 2D-FFT analyses—have the same micrometer-scale wavelength. These undulations are accompanied by a systematic out-of-plane displacement of the nanorods. Our results are discussed in the context of an earlier hypothesis that predicts pH oscillations near the biomorph crystallization front. In addition, we investigate the morphogenetic influence of inorganic dopants that compete with the barium carbonate crystallization and induce alternative growth mechanisms through amorphous precursors. Our observations highlight the importance of crystal structure in the assembly of these non-crystallographic biomorph shapes.

The use of organic matrices as a structural template for the bottom-up fabrication of organic-inorganic nanocomposites is a powerful way to build a variety of advanced biomaterials for hard tissue engineering. In contrast to metals and ceramics, polymeric matrices are much easier to be fabricated into diverse shapes. By controlling mineral deposition in the organic matrices, predictable morphology of the mineralized nanocomposites can be obtained. In this study, we designed and used elastin-like recombinamers (ELRs) in different shapes, electrospun nanofibers and 3D hydrogels, to template mineralization of hydroxyapatite nanocrystals using the biomimetic Polymer-Induced Liquid-Precursor (PILP) mineralization process. Different from conventional mineralization where minerals are nucleated and grown or deposited on the surface of organic matrices, the minerals were deposited within the framework of the ELRs, attaining high mineral density and mechanical properties to those of natural bone.

Unlike the classical nucleation theory, where crystal nucleation from a supersaturated solution occurs when a sufficiently large density fluctuation of the solution overcomes a free energy barrier between the crystalline and solution phase, calcium phosphate mineralization in PILP process proceeds via an amorphous precursor phase. The amorphous calcium phosphate precursor phase can infiltrate into organic matrices and replicate their original structures. ELRs are biosynthetic recombinant polypeptides based on repeating peptide sequences derived from tropoelastin, the most prominent being (VPG-Xaa-G), where Xaa is a guest amino acid (excluding proline).[16] One of the unique properties of these recombinamers is their inverse transition temperature (Tt) that allows them to transition between a soluble form, bellow Tt, and an insoluble aggregation in response to an increase of temperature above Tt. At the nanoscale, these ELRs self-assembled into 5 nm wide twisted filaments consisting of several β-spirals. These filaments were
aligned in parallel into fibrils with several hundred nanometers in diameter. The amorphous precursor nanoclusters might infiltrate into the nanocompartments between the ordered structures of the ELR framework and then coalesce, solidify and crystallize to form close-packed crystals. By designing the sequence of the ELRs and controlling the morphologies of ELRs matrices at different dimensional levels, diverse hybrid nanocomposites with optimized mechanical and biological properties can be constructed, suited for the treatment of bone defects using regenerative medicine approaches.

**4:45 PM - 5:00 PM**

**IDENTIFICATION OF ORGANIC NETWORKS WITHIN THE SKELETON OF REEF BUILDING CORALS: THE ROLE OF FUNGI IN THE ACCRETION OF ARAGONITE**

Zhan Wei-Scullion, Renee van de Locht, Peter J. Young, Henning Osholm, Remi Blanc, Roland Kroeger

1University of York, York, United Kingdom; 2University of Copenhagen, Copenhagen, Denmark; 3FEI Visualization Sciences Group, Paris, France

Stony corals such as those of the Porites or Acropora genera exclusively form their skeleton from the calcium carbonate polymorph aragonite and create the vast majority of the world’s reefs hosting approx. 25% of marine life. Despite great efforts the fundamental mechanism of the skeleton accretion remains a matter of intense discussion. Our work focuses on the possible correlation of organic inclusions found within the skeleton and the pathways by which the aragonite is created in corals. We particularly concentrate on the presence of marine fungi discussing whether they may play exclusively detrimental roles in the coral growth as pathogen or whether these microorganisms might provide support to the mineralization. The latter - beneficial - possibility arises from the X-ray tomography and electron microscopy (SEM and TEM) based observation of extended networks of organic fibers similar in size and morphologies to fungal hyphae within the matrix of the skeleton as well as aragonite crystals attached to the fibers found at the surface of the skeleton after removal of the polyp tissue. These fiber networks are observed throughout all investigated specimens and are not found to relate to well-known coral diseases. DNA analyses on different coral varieties indicate the presence of distinct fungi within different corals. On the basis of these findings the potential role of fungi in the control of coral mineralization is discussed. A detailed study of the microstructural evolution of the mineral phase around the fibers was performed using TEM on focused ion beam prepared cross-sections revealing that the ring pattern - characteristic for the diurnal coral growth - is caused by a periodic variation of the crystal morphology from randomly organized nanocrystals to acicular extended crystals leading to variations of light scattering and hence dark and bright banding [1]. We therefore hypothesize that fungi can play a role in the growth and structure formation of the coral skeleton.

systems will be presented, all inspired by their mineralogical roots. This includes many others that have obvious mineralogical roots, but there remains a great untapped potential for the crystal grower to explore. This untapped potential for the crystal grower to explore. This untapped potential for the crystal grower to explore.

Single crystals of relaxor-based perovskite solid solutions, namely PMN-PT, PZN-PT, and PIN-PMN-PT, exhibit excellent piezoelectric properties. However, these materials suffer from some inherent drawbacks such as low Curie temperature ($T_c$) and depoling temperature ($T_{dep}$; $\sim 100$ °C), and a low coercive field ($E_c \approx 3$ kV/cm), which prevent them from being used in high-power and high-temperature devices. To overcome these shortages, we have designed and developed single crystals of lead zirconate-titanate, Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT), and Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-based binary and ternary solid solutions, which are demonstrated to have high-$T_c$ and high piezo-/ferroelectric performance.

PbZr$_x$Ti$_{1-x}$O$_3$ single crystals with a wide composition range across the morphotropic phase boundary (MPB) ($0.20 \leq x \leq 0.65$) were successfully grown by a top-seeded solution growth (TSSG) technique. The crystal growth conditions are optimized in terms of the chemical, thermodynamic and kinetic parameters. The growth temperature is found to be a key factor for controlling the composition of the grown crystals. PZT crystals with composition from $x = 0.42$ to $x = 0.47$ show characteristic ferroelectric-to-ferroelectric phase transitions due to the presence of a curved MPB. The crystals of MPB composition, $x = 0.46$, are found to exhibit the best properties, with a piezoelectric coefficient $d_{33} = 1223$ pC/N, an electromechanical coupling factor $k_{33} = 0.8$, a large coercive field $E_c = 7$ kV/cm and a high Curie temperature $T_c = 386$ °C. The studies of the mesoscopic domains and local polar domain structure and the properties of the PZT crystals reveal unusual phase transition behavior with multiple tricritical points, and suggest that quenched random fields play an important role in the formation of nanodomains in PZT, which is discussed in the framework of the relaxor ferroelectrics.

Single crystals of the binary Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-PbTiO$_3$ [BZT-PT] and ternary Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$ [BZT-PZ-PT] systems were grown by the flux method, the top-cooled solution growth and the TSSG. The BZT-PT crystals display a $T_c$ as high as $550$ °C and a very large value of tetragonality ($c/a > 1.08$). The BZT-PZ-PT crystals exhibit pseudo-cubic morphology with dimensions of $2 \times 2 \times 0.5$ cm$^3$. The high ferroelectric $T_c$ is found to be $320$ °C. The largest remnant polarization of $32 \mu$C/cm$^2$ is displayed with an $E_c$ of $15.4$ kV/cm.

These results indicate that the BZT-PT, BZT-PZ-PT, and BZT-PZ-PT single crystals form a class of high-$T_c$ and high-performance piezoelectric materials potentially useful for high-power electromechanical transducers that can operate in a wide temperature range and at high fields.
Pyrochlore Pr2Zr2O7 single crystals have been studied to elucidate the dependence of their magnetic, compositional and structural properties on synthesis and growth conditions. All samples were characterized using X-ray diffraction, specific heat, and DC magnetization measurements. Stoichiometric and high quality single crystals of Pr2Zr2O7 were grown using the optical floating zone technique under a high purity static argon atmosphere, to avoid inclusions of Pr4+ and limit Pr vaporization. Increasing the growth speed was found to significantly reduce Pr vaporization for better control of stoichiometry. The magnetic susceptibility of crystals grown at rates from 1-20 mm/hr revealed changes that were consistent with Pr vaporization. Overall, the results clearly demonstrate important correlations between the growth conditions and physical properties of Pr2Zr2O7 crystals.

The Yb3+-doped LiB1-xYbx(WO4) fibers single crystals have been pulled using Micro Pulling Down technique with controlled diameter and stationary stable growth conditions, corresponding to flat crystallization interface with meniscus length equal to the fiber radii. The pulling rate range [2-6 mm h-1]. We have determined the monophased field of LiBi1-xYbx(WO4)2. The lattices parameters decrease as a function of Yb3+ substitution in Bi3+ sites. The characterization structural has been study by DRX and Loue method. The Raman, micro-luminescence characterizations have been performed. And Decay time has been drawn for the LBiW Yb3+ doped fibers and powder.
Friday, August 7, 2015
8:00 AM - 10:00 AM

Industrial Crystal Growth Technologies and Equipment (ACCGE) 5

Location: Madison
Session Chair(s): Govindhan Dhanaraj

8:00 AM - 8:30 AM
RECENT PROGRESS IN HYDROTHERMAL GROWTH OF CRYSTALS
Invited
K. - BYRAPPA¹, K. NAMRATHA²
¹MANGALORE UNIVERSITY, MANGALORE, India; ²UNIVERSITY OF MYSORE, CENTER FOR MATERIALS SCIENCE AND TECHNOLOGY, India

Hydrothermal method is one of the most important solution techniques of crystal growth known for its environmentally benign process and for high quality crystals. Although the technique started during the middle of 19th century as a part of silicate technology involving very high temperature and pressure conditions, but in recent years the method has become very popular and environmentally benign. The process parameters are well understood and have led to the reduction in the pressure - temperature conditions. The authors review the recent progress in the hydrothermal growth of crystals covering both bulk and small crystals. The method offers advantages for in situ surface modification and control over the size and shape of the crystals. In recent years, the thermodynamic calculations have facilitated to the successful growth of materials under controlled conditions predicted through the calculations. The authors present here the recent progress made in the hydrothermal growth of crystals with appropriate examples of technologically important materials like quartz, nitrides, oxides, etc.

8:30 AM - 8:45 AM
GROWTH AND PROPERTIES OF DOPED LANGASITE-TYPE LPE FILMS
Christine K. Rivenbank
Titusville, FL

Piezoelectric crystals of langasite-type family, La₃Ga₂SiO₁₁ (LGS), La₃Ga₅Ta₃O₁₄ (LGT), and La₃Ga₅Nb₃O₁₄ (LGN) have attracted significant attention because of their piezoelectric properties superior to quartz. For optimal performance of acoustic resonators of these materials in frequency-control and high-temperature sensing applications, maximization of the quality factor Q is necessary. In melt-grown LGS and LGT, point defect relaxation has recently been linked to acoustic losses, and a lower materials quality factor Q with increasing temperature (from 100K to 750K) than probably possible. Langasite-type LPE films have the potential of very high structural homogeneity, and an inherently lower concentration of native point defects, because they are grown at a lower growth temperature than corresponding crystals from the melt, and under near-equilibrium diffusion-controlled conditions. In this paper we present new results on liquid phase epitaxial (LPE) growth of in-situ co-doped langasite-type LPE films and their characterization. Co-doping opens possibilities in tuning film properties for given application. The crystalline perfection of the films was evaluated by rocking curve measurements, and compared to Czochralski-grown material. Ion-(co)implanted LGT substrates were used as standards for the quantitative determination of equilibrium dopant concentration by Secondary Ion Mass Spectroscopy (SIMS). Rutherford Back Scattering (RBS), in combination with SIMS, was also used to compare the nominal La-Ga-Ta stoichiometry of the films and substrates, and potential film contamination by solvent ions. The electrical and piezoelectric properties were investigated using impedance spectroscopy and resonance - antiresonance techniques. Piezoelectric properties of single crystal films grown by LPE and bulk crystals grown by Czochralski technique are compared, and the applicability of langasite-type piezoelectric material will be discussed.

8:45 AM - 9:00 AM
DIRECT DETERMINATION OF BURGERS VECTORS OF C AND NC+MA THREADING DISLOCATIONS IN 4H-SiC C-WAFERS GROWN BY PVT METHOD
Jianqiu Guo, Yu Yang, Fangzhen Wu, Huanhuan Wang, Balaji Raghothamachar, Michael Dudley
Stony Brook University, Stony Brook, NY

It is well-known that Threading Screw Dislocations (TSDs) are present in 4H-SiC crystals grown by Physical Vapor Transport (PVT) method. Recent studies [1] show that a significant proportion of these threading dislocations are actually mixed type dislocations with a Burgers vectors c+a or 1/3(11-23) type. With the help of Synchrotron White Beam X-ray Topography, it is easy to distinguish these threading c+a dislocations from pure screw dislocations simply by recording different reflections from an axially cut sample (cut parallel to growth direction) and applying g.b = 0 and g.b+.1 = 0 invisibility criteria (g - diffraction vector; b - Burgers vector). However, axial wafers are only cut from the boules slanted for research purposes and usually unavailable for boules from which commercially preferred c-plane oriented wafers are sliced. Therefore, in order to characterize the distribution of c and c+a threading dislocations in horizontally cut c-plane wafers, we present a new method to determine the Burgers vectors of threading dislocations. In this study, a 100mm 4H-SiC commercial wafer was used, from which all six 11-28 type grazing incidence reflections were recorded using Synchrotron Monochromatic X-ray Topography. Contrast was analyzed for threading dislocations on different reflections and compared to the simulated images of threading dislocations of possible Burgers vectors. Simulated images were obtained by Ray Tracing Simulation, which is based on the fact that orientation contrast is the predominant contributor to contrast from threading dislocations in the grazing incidence and back reflection geometries [2]. Burgers vectors of selected threading dislocations in this wafer were thus determined and the average ratio of c+a dislocations to pure c dislocation was then measured. Ray tracing simulations were also done for 1-109 type reflections and possibility of distinguishing threading c+a with pure c dislocations from these reflections will be discussed as well.
It is observed that a [0001] facet is formed on top of the boule during PVT growth of 4H-SiC. The facet region is visible as a central doping core with a darker contrast in c-plane wafers sliced from the N-doped 4H-SiC boule. This indicates the dopant concentration in the facet region is much higher than the rest of the boule. Using the synchrotron X-ray topography techniques, the detailed studies were carried out for the facet regions after the wafers from different boules has been subject to chemical mechanical polishing followed by high temperature heat treatment. The pile ups of double shockley stacking faults in the facet region were observed. The double Shockley stacking faults, which are bound by partial dislocations lying in the Peierls valleys along the <11-20> directions, are formed by the glide of two leading partial dislocations on adjacent basal planes. The contrast from the double shockley faults are found only in facet regions indicates that the requisite conditions for double shockley stacking faults formation are the presence of surface source, such as scratches, and a high enough N doping concentration, which is satisfied only within the facets. Additionally, the lowest minority carrier lifetimes compared to the rest of the wafer characterized by the lifetime mapping measurements also indicates the high density of stacking faults inside the facet regions.
Semiconductor nanowires (NWs) have stimulated interest in recent years because of their unique properties and potential applications as building blocks for nanoscale electronic and photonics devices. In this talk we report on the selective-area growth of vertical III-V compound semiconductor NWs on Si and Ge substrate and their device applications. In this talk, we briefly review the selective-area growth of III-V NWs and report on heterogeneous integration of vertical III-V NWs on patterned Si (111) substrates [1,2,3]. We used the specific growth sequence and modifying initial Si (111) surface into (111)B-polar surface in order to control the growth direction to vertical direction technique. The use of the technique enabled direct integration of vertical III-V NWs on Si and Ge(111) substrates. Cross-sectional transmission electron microscope images showed that lattice relaxation was suppressed with decreasing opening diameter.

Then we report on integration of GaAs NW-based light-emitting-diodes (NW-LEDs) on Si substrates. The vertically GaAs/AlGaAs core-shell multishell NWs with radial p-n junction and NWLED array showed that threshold current for electroluminescence (EL) was 0.5 mA (current density was approximately 0.4 A/cm²). This technology could open new possibilities for monolithic- and on-chip integration of III-V NWs on Si [4].

Finally, we demonstrate electronic devices using III-V NWs on a Si substrate. Fabricated vertical transistors contained InₓGa₁₋ₓAs NWs with modulation doped layer. We observed n-type FET behavior in Iₛ₋Vₛ and Iₓ₋Vₓ characteristics. The performances are threshold voltage − 0.25 V, Gₘₙₓₓ = 1.45 μS/μm at Vₛₓ = 0.50 V, Iₓₓ / Iₓₓ > 10⁶, subthreshold slope, SS = 80 mV/decade.

Besides the III-V NW-based vertical FETs, the heterointerface between the III-V NWs and Si can be used as tunnel FETs (TFETs).

In this case, we use band discontinuity between InAs NWs and Si substrate for TFETs. The device fabricated by InAs NW on Si substrate showed switching behavior with an average subthreshold slope (SS) of 30 mV/dec, which is much lower than the physical limitation of metal-oxide-semiconductor field-effect transistors (MOSFETs, SS ~ 60 mV/dec.) [5]


8:30 AM - 8:50 AM

GAAS CORE-SHELL NANOWIRE TUNNEL DIODES GROWN BY ORGANOMETALLIC VAPOUR PHASE EPITAXY
Ali Darbandi, Simon Watkins
Simon Fraser University, Burnaby, BC, Canada

Semiconductor nanowires (NWs) are promising candidates for various devices, including photovoltaics, tunneling field effect transistors, light emitting diodes, among others. This paper reports on the growth and electrical characterization of free standing GaAs single NW core-shell n-p structures and their characterization by a nanoprobe method in a scanning electron microscope. This technique can be used to measure an ensemble of NWs without their removal from the substrate, resulting in little surface damage compared with the usual lithographic methods.

NWs were grown by gold nanoparticles as a catalyst using organometallic vapour phase epitaxy (MOVPE). The method takes advantage of a novel hybrid growth technique using gallium oxide deposited by atomic layer deposition (ALD) over the Au nanoparticles. The gallium oxide is selectively desorbed only at the catalyst nanoparticle, ensuring that OMVPE growth only occurs at the NW preventing the formation of a parasitic p-n junction on the substrate surface. The n-type NW core was achieved using the precursor trimethylgallium (TMGa) at 400C and diethyltellurium for n-type doping up to 1E18/cm3. Growth interrupts were used to purge the Au nanoparticle of residual Te dopant prior to the growth of the p-type shell. Various thicknesses of intrinsic and p-type shells were achieved using triethylgallium (TEGa) to promote lateral growth, and diethylzinc for p-type doping. The p-type shell doping was estimated to be close to 1E20/cm3 based on resistance measurements of NW shells of known dimensions. The nanoprobe technique was used to measure the electrical properties of free standing coaxial n-p NW junctions on an n-type substrate. The n-type contact was provided by the GaAs substrate through the n-type core, whereas the p-type shell contact was obtained via a tungsten nanoprobe contacting the Au nanoparticle which formed an Ohmic contact to the degenerately doped shell. In highly doped junctions, radial tunneling transport was obtained. This is supported by the observation of negative differential resistance behaviour with peak-valley ratios up to 5.0. The ideality factors of the thermal region of these unpassivated devices were as low as 2.8. We present the effect of variations in NW doping, optimization of the core-shell geometry, surface passivation, and Ohmic contact formation via the Au nanoparticle.
Moneesh Upmanyu, Alireza Shahabi  
Northeastern University, Boston, MA  
The vapor-liquid-solid route for growth of semiconducting nanowires is mediated by a catalytic liquid droplet. The transition from supported droplet to a droplet-capped nanowire sets the nanowire diameter and orientation, and is therefore of considerable importance in scalable synthesis of nanowire arrays. Unfortunately, the transition remains poorly understood. Here, we perform atomic-scale computations on a supported AuSi droplet on a Si(111) substrate, subject to Si flux, and uncover the mechanistic details of the nucleation of nanowire. Our results show that the growth flux can destabilize the contact line and lead to droplet spreading via a nanoscale precursor foot. The resultant crystallization of the NW occurs over a much larger growth area, resulting in a much larger nanowire diameter. We present theoretical models to explain the instability of the droplet, and also the role of the Young's balance at the contact line during the nanowire nucleation.

9:10 AM - 9:30 AM  
GROWTH PARAMETER DESIGN FOR HOMOGENEOUS MATERIAL COMPOSITION IN TERNARY GaInP NANOWIRES  
Alexander Berg, Filip Lenrick, Neimantas Vainorius, L. Reine Wallenberg, Magnus T. Borgström  
Lund University, Lund, Sweden  
Objectives:  
* achieving a homogeneous materials composition in ternary GaInP nanowires  
* potential for using the nanowire core as a “substrate” for radial nanowires  
* avoiding lattice-mismatch between nanowire core and nanowire shell along the axial direction of the nanowire  
Method:  
Ternary GaInP nanowires (NWs) often exhibit an inhomogeneous materials composition along the NW growth axis because of different diffusion and decomposition properties of the precursors. This often leads to a wide variation in the composition range and corresponding luminescence of ternary NWs. Here, we present a method to overcome this challenge for GaInP NWs by linearly increasing the trimethylindium (TMI) molar fraction in situ during growth of ternary Zn-doped GaInP NWs while keeping the trimethylgallium (TMG) molar fraction constant. For synthesis of the GaInP NW arrays a SiNx growth mask was used which was patterned by nanoimprint lithography. The NW materials compositions from In rich to Ga rich were determined by use of x-ray diffraction (XRD) and scanning transmission electron microscopy electron dispersive x-ray spectroscopy (STEM-EDX) and the optical properties by photoluminescence (PL).  
Results:  
XRD results show a broad peak for the samples where TMI was kept constant during growth of the NW core. For the NWs where TMI was ramped, the XRD peaks were relatively sharp with a narrower full-width-at-half-maximum (FWHM). From STEM-EDX measurements we observe an increasing signal for Ga and a decreasing signal for In along the length of the NW grown with a constant TMI molar fraction. For the ramped TMI the Ga to In ratio is constant. With photoluminescence measurements we also find that the FWHM is narrower upon ramping TMI during growth, which indicates a more homogeneous materials composition.  
Conclusion:  
The results from XRD, STEM-EDX and PL show that the materials composition of Zn-doped GaInP NWs is inhomogeneous for the NWs which were grown with constant TMI. On the other hand, the composition becomes homogeneous as TMI is increased by about 25% in situ during growth for a growth time of 4 min.  
Outcomes:  
The findings of this study are promising for NW-based optoelectronic devices such as light-emitting diodes or solar cells in the radial geometry to avoid any strain effects between the NW core and a possible NW shell. This would increase the efficiency by avoiding dislocations and thus undesired non-radiative recombination.
DOPANT CHARACTERIZATION FOR GAN NANOWIRES BY RAMAN SPECTROSCOPY
Kris Bertness, Lawrence Robins, Shannon Duff, Paul Blanchard, Matt Brubaker, Norman Sanford
NIST, Boulder, CO

We apply Raman spectroscopy to characterize n- and p-type doping in GaN nanowires grown with catalyst-free molecular beam epitaxy. Ensembles of randomly nucleated, as-grown nanowires on Si substrates were doped with Mg or Si for p-type or n-type conduction, respectively. The nanowire ensembles were examined with a Raman system with a laser wavelength of 633 nm and back-scattered geometry. Because of the small size of the nanowires and the substantial effects of surface depletion regions, electrical measurements of carrier concentration and mobility suffer from large uncertainties. By measuring the peak frequency or normalized intensity of specific Raman peaks, the absolute carrier concentration (in n-type GaN) or relative active dopant concentration (in p-type GaN) can be estimated independently of the electrical properties. Specifically, for n-type doping, the shift of the longitudinal optical (LO) phonon peak near 739 cm\(^{-1}\) due to coupling with plasmon modes of the free carriers may be analyzed to estimate carrier concentration. This coupled LO-phonon-plasmon (LPP\(^+\)) peak upshifts approximately 8 cm\(^{-1}\) for carrier concentration of 3 × 10\(^{17}\) cm\(^{-3}\). For p-type doping, we analyze a Raman peak with characteristic shift of approximately 655 cm\(^{-1}\) that has been shown to arise from N-Mg bonds in the correct lattice position for doping and in the absence of hydrogen passivation. To compensate for variations in the specimen volume probed by Raman, the Mg peak intensity is normalized by the total signal measured for the strong TO and E\(_2\) peaks of GaN in the range of 520 cm\(^{-1}\) to 580 cm\(^{-1}\). By comparing the normalized peak intensities for several Mg-doped nanowire ensembles and thin films, we find that Mg incorporation and activation increase with decreasing growth temperature and with increasing N:Ga flux ratio.
protocoll processes: 1) an equilibrium population of clusters in solution deposits onto the surface, 2) the deposited clusters transform and sheet stabilization. The assembly pathways on mica surfaces were observed using in situ atomic force microscopy (AFM) and shown to self-assemble into 2D or 3D structures ranging from bi-layer sheets to fiber arrays to porous networks. The molecular arrangements of these structures were determined by XRD and molecular simulations were revealed the structural source of fiber and sheet stabilization. The assembly pathways on mica surfaces were observed using in situ atomic force microscopy (AFM) and related to solution species observed through dynamic light scattering and TEM. During the assembly of porous networks from 12-mer di-block peptoids, 3nm-high “proto-fibers” were found to be the basic building blocks. These extended laterally to create an initial 3-fold symmetric array of fibers one molecule in width, but grew outward in 3nm increments to form 3D porous networks. However, nucleation of the proto-fibers occurred through transformation of 5Å high clusters having no apparent order and coexisting with monomers. Moreover the dependencies of cluster and proto-fiber number density were highly non-linear and changed dramatically with addition of a second hydrophobic region and the surface species co-existed with solution species. A kinetic model based that accounts for deposition and transformation of species provides an excellent fit to the data by assuming four basic processes: 1) an equilibrium population of clusters in solution deposits onto the surface, 2) the deposited clusters transform into proto-fibers while, 3) the solution clusters start converting into proto-fibers after an incubation period, and 4) deposit on the surface.
Based on these results, we propose a quantitative model to describe peptoid self-assembly and show how modification of the peptoid structure by introduction of the hydrophobic tail alters the incubation period and rate coefficients that control assembly. The results demonstrate that, even for these relatively short macromolecular sequences, assembly follows a hierarchical pathway the outcome of which can be well-understood using existing molecular simulation techniques with appropriate potentials.

9:30 AM - 10:00 AM
CRYSTAL NETWORKS IN SPIDER AND SILKWORM SILKS: FROM HIERARCHICAL STRUCTURE TO ULTRA-PERFORMANCE
Invited
Liu Xiang Yang
Singapore

This talk will be focused on the structural characteristics of crystal networks of fibrous soft materials in correlation with the macroscopic properties/performance, and the network formation mechanisms. The correlation between the hierarchical mesoscopic structures and the mechanical properties of silk fibrous soft materials including silk fibroin hydrogels and naturally spun silk fibers are addressed based on the hierarchical crystal network models. Namely, two types of hierarchical networks are identified: the weak nanofibril-nanofibril interaction case (i.e. silk fibroin hydrogels), and the strong nanofibril-nanofibril interaction case (i.e. silk fibers), respectively. The macroscopic properties, i.e. the rheological/mechanical properties, can be controlled in terms of tuning different levels of hierarchical network structures by ultrasonication-induced gelation, introducing the initial nucleation centers, etc. Such controls take effect by different meso-scale assembly pathways, which are found to occur via different routes of the nucleation-growth processes. Furthermore, the hierarchical network model of soft materials can be applied to explain the superior mechanical properties and the unique strain-hardening behaviors of spider silk fibers within the framework of hierarchical breaking mechanism. Evidently, the knowledge on crystal networks will allow the prediction of the performance of soft materials in generals and engineering strategy.

References
CRYSTAL GROWTH AND CHARACTERIZATION OF MGSIP2: A WIDE BAND GAP SEMICONDUCTOR FOR NON-LINEAR OPTICS

Lakshmi Krishna, Eric S. Toberer, Reuben T. Collins, Adele C. Tamboli

1 Colorado School of Mines, Golden, CO
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The large birefringence exhibited in II-IV-V2 ternary chalcopyrite semiconductors has attracted significant attention for technological applications involving non-linear optics. However, the investigation has extensively focused only Zn or Cd containing chalcopyrites whereas Mg containing chalcopyrites remain relatively unexplored [1]. Structurally, MgSiP2 has the largest tetragonal compression of any II-IV-V2 chalcopyrite compounds and the strongest displacement of anion from the tetrahedral position thereby providing an interesting opportunity to explore the non-linear optical properties of the compound [2]. In addition, this compound is also made of earth abundant, non-toxic elements. To investigate the optical properties of MgSiP2, growth of high quality and sufficiently large single crystals are desired.

In this work, we discuss the synthesis techniques to grow single crystals of MgSiP2 by flux technique. Stoichiometric amounts of starting material was taken in a Graphite crucible along with 95 mol. % excess Sn as a flux. The graphite crucible was placed in a quartz crucible and sealed under vacuum and heated to 1100 °C and subsequently cooled down to room temperature. MgSiP2 crystals obtained via this technique are bright orange in color and range in size (length) from few mm to a cm. The crystals are stable in air and can be etched in acidic solutions. Energy dispersive spectroscopy performed on the crystals confirms the stoichiometry to be close to MgSiP2. Experimental Raman spectroscopy data was acquired on the crystals for the first time and the spectrum is compared to the predicted pattern [3]. There is an excellent agreement between the experimental and theoretical data for wavenumbers below 360 cm\(^{-1}\), whereas, approximately a 25 cm\(^{-1}\) increase in the Raman shift is observed for peaks beyond 400 cm\(^{-1}\).

References
Low-temperature solution growth is the simplest, and in many cases, the least expensive method for production of optical crystals. However, its use for growth of large, commercially important single crystals has been so far limited to a few inorganic water-soluble materials, examples of which include Rochelle salt, triglycine sulphate, or potassium dihydrogenphosphate (KDP). For organic crystals, not soluble in aqueous solutions, the preference has been given to alternative methods, among which the Bridgman technique is the most common. Modern availability of commercially produced high-purity organic solvents and recent development of accelerated techniques for solution growth enables wider variations of growth methods to produce crystals of different materials. When large volumes of single crystal materials are needed for certain applications, solution growth methods may offer the advantage of easier scale-up. For organic crystals, one such application relates to their use in scintillation devices that deploy fluorescent properties of organic crystals enabling efficient neutron detection in the presence of gamma radiation. The present paper will describe growth of large (~10 cm scale) single crystals of pure aromatic hydrocarbons, trans-stilbene, 9,10-diphenylanthracene, diphenylacetylene, and bibenzyl, as well as crystals of aromatic compounds containing metal atoms (Li, Cs) in their composition. Growth mechanisms and measures to prevent specific defect formation will be discussed to show that under controlled conditions solution growth produces crystals of higher structural perfection and better optical quality in comparison to the same crystals grown by traditional melt techniques. With large variety of unexplored organic crystals, the results of the studies indicate new pathways for production of novel materials for different applications.
SYNTHESIS GROWTH OPTICAL AND MECHANICAL STUDIES ON UREA OXALIC ACID FERROELECTRIC SINGLE CRYSTAL
Ezhil Vizhi R, Dhivya Immanuel, Rajan Babu D
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Single crystal of urea oxalic acid was grown by slow evaporation method. The lattice parameters such as a = 5.13 Å, b = 12.48 Å, c = 7.07 Å and it belongs to monoclinic system with space group P21/c were calculated using single crystal X-ray diffraction analysis. Ultra Violet-Visible spectrum was recorded from the wavelength region of 200 - 800 nm and its cutoff wavelength was found to be 270 nm, optical energy band gap 4.57 eV was determined by using Tau’s plot relation. The various parameters such as extinction coefficient, reflectance values were calculated by using standard relations. The presence of N-H asymmetric stretching occurs at 3444 cm⁻¹ and 1853 cm⁻¹ due to the amide C = O symmetric stretching was confirmed by Fourier transform infrared vibrational spectrum analysis. The existence of hydrogen and carbon atoms were confirmed by Fourier transform nuclear magnetic resonance analysis. The mechanical stability of the grown crystal was estimated by Vickers micro hardness studies and the material belongs to hard material category. Hardness related parameters such as elastic stiffness constant, fracture mechanics, brittleness index and also yield strength were evaluated.

References

INVESTIGATIONS ON THE GROWTH ASPECTS AND PROPERTY STUDIES OF γ-GLYCINE SINGLE CRYSTAL IN THE PRESENCE OF SODIUM BROMIDE
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Organic nonlinear optical material of γ-glycine single crystal in the presence of potassium bromide [1] and Triglycine sulfate doped sodium bromide [2] were grown by slow evaporation method and its characteristics such as structural, optical, thermal and SHG studies were investigated. To the best of our knowledge there is no report the growth of gamma glycine in the presence of sodium bromide. Hence in this paper we have presented the growth aspects and property studies of γ-glycine single crystals in the presence of sodium bromide for the first time. Solubility of the material was analyzed gravimetrically. The grown crystal possesses positive temperature coefficient of solubility. Metastable zonewidth was studied by polythermal method. The grown crystals have also been subjected to Powder X-ray diffraction study to identify the crystalline nature. The lattice parameters were calculated and the values are a = b = 7.06 Å, c = 5.31 Å and V = 230 Å³. Thus the grown crystal belongs to hexagonal system. The presence of all the functional groups of the γ-glycine was confirmed by Fourier - Transform Infrared (FT-IR) and FT-Raman spectral analysis. Thermal properties of the grown crystal was done by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA), which
indicates the thermal stability and their melting point. The mechanical studies of the grown crystal was subjected to Vickers microhardness test. The result shows the hardness number increases with increasing load exhibits the reverse indentation size effect. The dielectric response of the sample is studied as a function of frequency and temperature. The optical transmission was ascertained by UV-Vis-NIR analysis, it shows that the lower cutoff wavelength is 224 nm and energy band gap value was found to be 5.5 eV. The second-order nonlinear optical property was analyzed by Q-switched Nd:YAG laser technique and SHG efficiency of γ-glycine is comparable that of KDP.

Reference

Transmission Spectrum of Gamma Glycine

A REPORT ON THE BULK SIZE CRYSTAL GROWTH OF MMTC BY A NOVEL AND SIMPLE SOLUTION GROWTH TECHNIQUE AND THEIR CHARACTERIZATION
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Abstract
In the present work, golden yellow coloured bulk size (27x13x11 mm³) non-linear optical single crystal of manganese(II) mercury(II) tetra thiocyanate (MMTC) was conveniently grown from the mother solvent using a novel and simple solution growth technique. The bulk size growth of MMTC by the simple and modified crystal growth setup and growth procedure has been described for the first time. The grown crystals were also subjected to SXRD, HPLC, FT-IR, FT-Raman, Confocal Raman, UV-Vis-NIR, TG-DTA, DSC, SEM, VSM and temperature dependent ESR studies and the results are presented. The ESR spectral profile of the complex MMTC is symmetrical on both side of the central field at 295 K, which suggests that the environment of Mn ions is symmetrical with respect to the SCN ligand. In addition, hyperfine interaction between the nucleus and the electron is absent. The absence of hyperfine interaction is ascribed to delocalization of Mn d⁵ electrons over the thiocyanate ligands. Even with the decrease in temperature from 295 to 110 K, hyperfine interaction was not observed. The thermal stability of MMTC in nitrogen atmosphere is found to be 371.17°C.
Methods: An indenter array, which is fabricated spatially high degree of spatial and size uniformity would impact numerous technologies, in
Objectives: The ability to scalably fabricate periodic, large
1
STRESS
11:10 AM
with threshold current densities of 160 A/cm² and 260 A/cm² (1000 ns) to reduce self
The processed 2 mm long, 50
of 39 nm. The latter indicates a higher degree of compositional and size inhomogeneity of InPAs QDs.

binary InP QDs was dominated by an emission centred at 716 nm with a full width at half maximum (FWHM) of 22 nm. Adding
built around a polaron cell where the light was collected through the top p-type GaAs cap layer. The LCL spectrum of the nominally
area growth
-324 nm by slicing the nanocolumns horizontally at a height of ~300 nm above their bottoms and dislocation propagation through the nanocolumns was analyzed by the cross-sectional TEM
-200 nm. It was clarified that dislocations were effectively filtered in the bottom 300 nm region of the nanocolumns, the occurrence probability of dislocation-free nanocolumns increased with decreasing D, and for narrow nanocolumns with D< 200 nm, dislocation-free crystals were obtained in the upper part of the nanocolumns, as shown in Fig. 2. The
dramatic improvement in the emission properties of GaN nanocolumns observed with decreasing diameter is discussed in relation to the decreased dislocation density. The laser action of InGaN/GaN-based nanocolumn arrays with a nanocolumn diameter of 170 nm and a period of 200 nm on Si under optical excitation was obtained with an emission wavelength of 407 nm. We also fabricated red-emitting InGaN-based nanocolumn LEDs on Si that operated at a wavelength of 652 nm, demonstrating vertical conduction through the AIN/GaN SL buffer to the Si substrate.

10:50 AM - 11:10 AM
INPAS/ALGAINP/GAAS QUANTUM DOT LASER STRUCTURES GROWN BY MOVPE
Andrey Krysa1, John Roberts1, Thomas Walther1, Ivan Karomi1, Samuel Shutts1, Peter Smowton1
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Recently, InP QDs grown in AlGaN matrices on GaAs substrates have shown a significant potential for optoelectronic and spintronic applications. In particular, InP QD based low threshold laser diodes, semiconductor disc lasers, microcavity structures, semiconductor absorber mirrors, single-photon emitters and long living nuclear spin states in InP QDs have been demonstrated. Adding arsenic to InP QDs lowers the bandgap of the dot material and increases the lattice mismatch in respect to GaAs substrates, and, thus, offers extra flexibility in engineering the above QD structures and allows extending their spectral operation range towards longer wavelengths in the near infra-red band.

In this research, we applied a fairly standard (for manufacturing AlGaN-based red lasers) MOVPE process, including commonly used group V precursors, i.e. arsenic and phosphine, for InPAs QD growth, and demonstrated the feasibility of this approach to extend the QD laser operation towards longer wavelengths. The active region of the laser structures consisted of 5 InP or InPAs QD sheets with a GaN quantum well with a thickness of 8 nm grown above each QD sheet and separated by a layer of (Al0.3Ga0.7)0.52In0.48P with a thickness of 16 nm. The intended fraction of arsenic in InPAs QDs was ~20%. The active region was sandwiched with a Al0.52In0.48P clad / (Al0.3Ga0.7)0.52In0.48P core waveguide.

Prior device processing, the as grown epi-wafers were examined using a pulsed current liquid contact luminescence (LCL) setup built around a polaron cell where the light was collected through the top p-type GaAs cap layer. The LCL spectrum of the nominally binary InP QDs was dominated by an emission centred at 716 nm with a full width at half maximum (FWHM) of 22 nm. Adding arsenic to the reactor during the QD growth resulted into a wavelength shift of the QD emission to 770 nm and an increased FWHM of 39 nm. The latter indicates a higher degree of compositional and size inhomogeneity of InPAs QDs. The processed 2 mm long, 50 μm wide, oxide isolated stripe lasers with uncoated facets were operated in pulsed mode (1 kHz, 1000 ns) to reduce self-heating. Both, InP and InPAs QD samples delivered up to 50 mW of optical powers at room temperature with threshold current densities of 160 A/cm² and 260 A/cm², respectively, and lased up to at least 370 K.

11:10 AM - 11:30 AM
STRESS-DIRECTED COMPOSITIONAL PATTERNING FOR RESPONSIVE SIGE SUBSTRATES
Talid Sinno1, Daniel Kaiser1, Swapnadip Ghosh1, Sang M. Han2
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Objectives: The ability to scalably fabricate periodic, large-area assemblies of Ge quantum dots (QDs) on Si or SiGe substrates with high degree of spatial and size uniformity would impact numerous technologies, including nano-/micro-electronics, optoelectronics and nanosensor arrays. Here, we describe a process in which SiGe substrates are compositionally patterned over large areas using spatially-modulated elastic fields.

Methods: An indenter array, which is fabricated by interferometric lithography and dry etching, is pressed against a Si0.8Ge0.2
wafer in a custom-made mechanical press. The entire assembly is then annealed at high temperatures, during which the larger Ge atoms are selectively driven away from areas of compressive hydrostatic pressure. A multiscale computer simulation approach also is developed. The model is based on a combination of lattice kinetic Monte Carlo (LKMC) and static energy minimization. The LKMC simulation is propagated using rates for atomic diffusion that depend explicitly on local values of stress, composition, and temperature. The stress field is updated quasi-statically using a separate energy minimization routine with forces computed based on a Tersoff interatomic potential for the Si-Ge system [J. Tersoff, Physical Review B 39, 5566 (1989)].

Results: Compositional analysis of the substrates demonstrates that this approach leads to a transfer of the indenter array pattern into the near-surface compositional distribution, which in turn induces a patterned surface stress. We use high resolution electron microscopy coupled with energy dispersive spectroscopy to image the compositional distribution for several different cases and show that elastic stress is crucial for achieving compositional patterning, while plastic deformation inhibits the effect. Using our computer simulation model we show that the residual surface stresses induced by compositional patterning is quite large, and also stable with respect to additional annealing. We also compare our results to the experimental measurements.

Conclusion and Outcomes: The approach described here is a potentially efficient, scalable, and versatile pathway for producing semiconductor surfaces that are patterned in both composition and stress. The stress modulation may be sufficient to break symmetry during subsequent molecular beam deposition of Ge, and thus may provide an efficient approach for producing highly ordered Ge quantum dot structures via the well-known Stranski-Krastanov heteroepitaxial growth mechanism. Moreover, the compositional variation, if sufficiently well harnessed could be used to directly engineer devices.

11:30 AM - 11:50 AM
EPITAXIAL QUANTUM DOTS ON NANOWIRES AND NANOPARTICLES: STABILITY AND GROWTH
Moneesh Upmanyu
Northeastern University, Boston, MA

Using theoretical analyses and simulations, we study the stability and growth of heteroepitaxial quantum dots on nanowires (NWs) and nanocrystals (NCs). In each case, the quantum dot formation is governed by the well-known Asaro-Tiller-Grinfeld (ATG) instability due to the competition between the bulk elastic energy and surface energy of the strained epilayers. Our studies show that the stability is modified by surface stresses and by the size of the NW/NC. By increasing the nanowire/NC size, transitions from formal growth to ordered quantum dots on the facets and further to ordered quantum dots on the corners take place. Our results have implications for self-assembled growth of size-controlled quantum dots for a wide range of applications.
There is an alarming increase of pollutants being discharged into the atmosphere and water. This is predominantly due to the increased use of fossil fuels as well as the rapid emergence of technological developments within industries (e.g., pharmaceuticals). Solar-based technologies offer efficient pathways to solving these issues. Titanium Dioxide (TiO₂) is an abundant, inexpensive semiconducting material that can be used to split water (forming hydrogen fuels) and completely mineralize organics without harmful byproducts. TiO₂ is synthesized by various methods such as chemical and physical vapor deposition, which require high temperatures or extreme atmospheric conditions to achieve the desired phase and size of the material. Mineralizing biological organisms demonstrate how elegant structures with controlled size, phase and orientation can be produced at room temperature through controlled organic-mineral interactions. These interactions are both chemical and structural in nature, exerting control over supersaturation as well as mineral alignment. Here, we are inspired by these control mechanisms to synthesize both highly oriented titanium dioxide nanowire arrays for water splitting and nanoporous membranes for water purification. The nanowire arrays were produced on polycrystalline TiO₂ templates via hydrothermal reactions. The effects of the reaction conditions and the properties of the templates on the TiO₂ nanowires are extensively investigated and discussed. Wires grow in an epitaxial manner, with their orientation dependent on the underlying TiO₂ grain. The diameter and the number density of the nanowires were tuned by controlling the surface properties of the templates, while the tip sharpness of nanowires was influenced by precursor solubility and diffusivity. Photoelectrochemical (PEC) performance of resultant TiO₂ nanowires for water splitting demonstrated the photocatalytic activity was dependent on the length and areal density of the nanowires, which was controlled by the synthesis conditions and the surface chemistry of the templates. Nanoporous membranes were synthesized using biologically-inspired scaffolds to template the nucleation and growth of TiO₂ with controlled size and phase. By modifying solution conditions, we have produced a self-supporting porous, high surface area TiO₂ nanoparticle membrane with controlled crystallite size, phase, and porosity. These bulk porous TiO₂ membranes can be utilized in photocatalytic applications, eliminating the need for nanoparticle recovery systems, thereby reducing processing costs and increasing amount of viable applications of photocatalytic systems.

Recent evidence reveal the presence of nanoscale mineral precursors that are intermediate phases in mineralization; clustering into assemblies that template for nucleation events. Several groups have shown that interactions with these intermediate phases drive mineralization along diverse pathways. These intermediate phases support the existence of a non-classical route to crystallization. We demonstrate that specific macromolecules found in Nature interact with these intermediate phases to select crystal polymorphs and form unique bulk crystalline arrangements. By regulating these interactions through physicochemical and microfluidic methods, we show that these macromolecules alter local ion supersaturation to drive mineralization along pathways that form specific mineral-organic assemblies. The characteristics of these assemblies are crucial in their regulation of nucleation and crystal growth mechanisms. With these observations, we can begin to formulate approaches that utilize these biological strategies in creating synthetic, bulk functional crystalline materials with tunable materials properties.

In order to allow both structure-guided drug design and controlled drug delivery, it is important to determine the 3D structures of protein molecules. At present, these structures are primarily determined using X-ray diffraction (XRD) analysis, and therefore high-quality single crystals of proteins are required, even though these are quite difficult to obtain. This is attributed to two difficulties: i) it is difficult to occur the nucleation for proteins, and ii) it is difficult to grow high-quality single crystals of proteins. Therefore, the development of crystallization techniques to control the nucleation rate and crystal quality of protein crystals is highly desirable. We have successfully achieved both an increase and a decrease in the nucleation rate of protein crystals by applying an external alternating current (AC) electric field, by focusing on the magnitude of the electrostatic energy added to the chemical potentials of proteins.
the liquid and solid phases 1), 2). At present, therefore, we have concentrated on improving the crystal quality of protein crystals under application of an external AC electric field. Recently, we have demonstrated that the full width at half-maximum (FWHM) values for X-ray rocking curves for tetragonal hen egg white (HEW) lysozyme crystals prepared in a 1 MHz external electric field are smaller than those obtained without application of the field 3). This suggests that the local crystal quality of tetragonal HEW lysozyme crystals may be improved by the application of an external electric field at 1 MHz. In this presentation, we discuss the origin of the improvement of the crystal quality in the light of the subgrain misorientation in the crystal.

Reference