ACCGE-23/OMVPE-21

Abstracts

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Poster

Growth of Single Crystal Fibers for Laser Applications

Allen Benton (Clemson University), **Joseph Kolis** (Ryan Terry)

Keywords: Growth; Oxides; LHPG; Optical; Optical Materials

Various Applications of Single Crystal Fibers for Lasing applications will be discussed. Specific attention will be placed on single crystal Lu_2O_3 fibers.

Invited Talk

Development and scale-up of n-type conductive SiC for power electronics applications

Ian Manning (SK Siltron CSS), **Sungchul Baek** (SK Siltron CSS), **Taehee Kim** (SK Siltron CSS), **Dowon Song** (SK Siltron CSS), **Meongkeun Ju** (SK Siltron CSS), **Andrey Soukhojak** (SK Siltron CSS), **Vladimir Pushkarev** (SK Siltron CSS), **Kevin Moeggenborg** (SK Siltron CSS), **Tawhid Rana** (SK Siltron CSS), **Matthew Gave** (SK Siltron CSS), **Gil Chung** (SK Siltron CSS), **Edward Sanchez** (SK Siltron CSS)

Keywords: Defects, Growth, Technology/Equipment; Bulk; Carbides; PVT; UWBG/WBG Semiconductor; Energy Materials

Over the past few decades, SiC has emerged as a leading material for substrates used in the fabrication of power electronic devices. Its wide bandgap and high thermal conductivity enable operation of such devices at high temperatures, and help mitigate the need for separate cooling modules, giving it distinct advantages for integration into hybrid electric vehicle inverters, charging stations, and other high temperature applications for which silicon has been the dominant substrate material. As with silicon, many technical and engineering challenges have been encountered with increasing commercialization and evolving customer needs. In particular, SiC manufacturers have devoted considerable effort to maintain bulk crystal yields, continuously reduce dislocation densities, and reduce in-grown stresses, while both scaling up volumes and increasing crystal diameters to achieve up to 200 mm wafers. This presentation details the industrial scale-up of n-type conductive SiC wafer production at SK Siltron CSS, with attention to key process developments and innovations leading to improvements in crystal size and quality. The impacts of modifications to the growth cell, in-furnace process parameters, and post-growth thermal treatment on these outcomes are discussed.

Invited Talk

Manufacturing 2-inch AlN and beyond: the road to 4-inch AlN substrates

Justin Mark (Crystal IS), **Robert T**. **Bondokov** (Crystal IS), **Kasey Hogan** (Crystal IS), **Griffin Q**. **Norbury** (Crystal IS), **James Grandusky** (Crystal IS)

Keywords: Characterization, Growth; Bulk; III-Vs (Traditional), Nitrides; PVT; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

The 2-inch crystal growth process for AlN has been significantly developed over the past decade. Currently, Crystal IS produces multiple thousands of high quality 2-inch AlN substrates per year. These substrates have demonstrated symmetric (0002) X-ray rocking curve FWHM values as low as 6.7 arcseconds, low UV absorption coefficients of ~10 cm-1 at 265 nm, and high room temperature thermal conductivities of 294 W m-1 K-1. These 2-inch substrates have thrived in the UVC LED market and the demand for larger substrates has grown with the anticipation for power electronic applications. In 2022, Crystal IS demonstrated similar quality 3-inch AlN and has since continued to expand to the 4-inch diameter, the desired size for next generation applications. We demonstrate the growth of 4-inch diameter AlN boules and their subsequent wafer characterization, signaling the first commercially available 4-inch substrate to be in the near future.

Invited Talk

Template-Assisted Selective Epitaxy of InAs on W metal films

Johannes Svensson (Lund University, Electrical and Information Technology), **Patrik Olausson** (Lund University), **Heera Menon** (Lund University), **Erik Lind** (Lund University), **Mattias Borg** (Lund University)

Keywords: Characterization, Growth; Low Dimensional; III-Vs (Traditional); VPE; Narrow Semiconductor; Optical Materials

3D integration of III-V semiconductors with Si CMOS is highly attractive since it allows combining new photonic and analog functions with digital signal processing circuitry. For example, in emerging 6G wireless networks, III-V devices such as high electron mobility transistors (HEMTs) or high-speed photodetectors monolithically integrated on top of Si CMOS circuitry can reduce footprint, minimize latency and allow optimal heat dissipation. Thus far, most 3D integration approaches have used epitaxial growth on Si, layer transfer by wafer bonding or die-to-die packaging. Here we present low temperature integration of InAs on W using Si3N4 template assisted selective area metal organic vapor phase epitaxy (MOVPE). Since the W metal can be deposited on any surface using sputtering, this method allows for III-V integration higher up in the CMOS stack as well as on non-crystalline substrates. Despite that the InAs is nucleating on polycrystalline W, we can obtain a high yield of single crystalline InAs nanowires for diameters below 75 nm, as observed by transmission electron microscopy (TEM) and electron back scatter diffraction (EBSD). For larger diameters, the yield of single grain nanowires decreases due to multiple nucleation sites on the W at bottom of the Si3N4 template openings. Electrical characterization, using a top metal contact and the growth template as a spacer, show that the InAs crystals exhibit a low-resistive, ohmic electrical contact to the W film even at cryogenic temperatures. The resistivity increases with template diameter which can be attributed to increased grain boundary scattering. MOSFETs have been fabricated from nanowires broken off and transferred from the growth substrate to enable field effect mobility extraction. These results demonstrate the feasibility for single-crystalline III-V back-end-of-line integration with a low thermal budget compatible with Si CMOS.

Invited Talk

GaAs solar cells on V-groove Si substrates

Theresa Saenz (National Renewable Energy), **Jacob Boyer** (National Renewable Energy Lab), **John Mangum** (National Renewable Energy Lab), **Anica Neumann** (National Renewable Energy Lab), **Sarah Collins** (National Renewable Energy Lab), **Michelle Young** (National Renewable Energy Lab), **Myles Steiner** (National Renewable Energy Lab), **Ryan France** (National Renewable Energy Lab), **Bill McMahon** (National Renewable Energy Lab), **Jeramy Zimmerman** (Colorado School of Mines), **Emily Warren** (National Renewable Energy Lab)

Keywords: Defects, Devices, Growth; Thin Film; III-Vs (Traditional), Silicon; CVD; Energy Materials

With the substrate making up as much as 80% of the total cost of a III-V solar cell [1], there have been recent efforts to develop methods to re-use III-V substrates or to replace them with alternative, low-cost substrates. One option is to use Si as the epitaxial substrate. III-V/Si tandem solar cells have theoretical maximum efficiency of 44% [2], and Si is already used at scale to produce solar cells. However, the direct epitaxy of III-V material on Si comes with a number of material quality challenges, including antiphase boundaries, threading dislocations, and cracking. V-groove Si, an approach where nanoscale patterning is used to selectively etch (111)-faceted trenches on a (001)-oriented wafer, has been used as a epitaxy substrate to demonstrate high quality epitaxial III-V growth, and is also interesting as a low-cost alternative to epi-ready polished wafers. In this talk, I will discuss the development of GaAs solar cells grown directly on V-groove Si substrates by MOVPE. III-V epitaxy on V-groove Si substrates has a number of unique materials science constraints not present for planar Si substrates. With the potential for both (111) and (001) planes to be exposed on the V-groove Si substrate prior to growth, the initial III-V nucleation process must be optimized to be facet-selective, in addition to the typical requirements for uniform morphology and high material quality. We have developed a nucleation process for growing GaP, which has a relatively small lattice mismatch to Si, on V-groove Si. We show that a high V/III ratio and temperature produces uniform GaP nucleation at the bottom of the V-groove trenches, which is necessary for minimizing crystalline defect formation. For solar cells, the III-V material must be coalesced into a thin film upon filling the V-groove trenches, which requires unusual growth conditions and a detailed understanding of how the nanopattern can affect the epitaxy. We demonstrate the ability to coalescence GaP into a thin film with a roughness of 0.2 nm and then produce GaAs thin films on that GaP/V-groove template with a threading dislocation density of 3Ã—10^6 cm-2. This talk will emphasize lessons learned about epitaxy on these non-standard substrates. Topics will include the use of AsH3 pretreatment annealing to control GaP nucleation facet selectivity, the role of Si in controlling GaP morphology through the coalescence process, and the management of misfit dislocations induced by threading dislocation glide during cool down. [1] J. S. Ward et al, Prog. Photovolt.: Res. Appl., vol. 24, pp. 1284â€“1292, 2016. [2] T. J. Grassman, et al, IEEE J. Photovolt.., vol. 6, no. 1, pp. 326â€“331, 2016.

RELIABLE BURIED HETEROSTRUCTURE LASER via AN MOCVD IN-SITU ETCH PROCESS

Anthony SpringThorpe (National Research Council Canada), **Omid Salehzadeh Einabad** (National Research Council Canada), **Muhammad Mohsin** (National Research Council Canada), **Grzegorz Pakulski** (National Research Council Canada)

Keywords: Characterization, Devices, Growth; Thin Film; III-Vs (Traditional); VPE; direct bandgap; Optical Materials

Buried heterostructure (BH) lasers are coherent light sources, with efficient operation at high temperatures, and with a low power consumption. The reliability of complex optoelectronic modules depends predominantly on the reliability of the laser components. The reliability of the BH lasers is dependent on both the design aspects, and the details of the fabrication process. In the presentation we will discuss the reliability issues related to the fabrication process, emphasizing the etching of the narrow mesa, and the overgrowth of the blocking layers. Previously1, we reported a successful process to etch various quaternary InGaAsP compounds in an MOCVD reactor, and described some initial results of InGaAsP based BH laser structures. We have recently extended our MOCVD in-situ etch capability to include the InGaAlAs material system. Furthermore, we have utilized our developed MOCVD â€˜in-situâ€™ etch technique to fabricate BH lasers. Here, we will show that the use of an MOCVD in-situ etch process, immediately followed by the growth of the blocking layers in a single MOCVD run, significantly improves the uniformity and reliability of the InGaAsP and InGaAlAs MQW BH lasers, as well as for InAs QD BH lasers. The results of the accelerated aging on threshold current degradation will be discussed. Reference 1 Comparative study of â€™in-situâ€™ etching of InP-based Quaternary alloys in an MOCVD reactor, A. J. SpringThorpe and O. Salehzadeh Einabad - Presented at CSW Stockholm May 2021. Figure 1. SEM cross-section image of a fully processed BH laser device. Figure 2. CW LIV characteristics of 24 BH FP lasers measured at 20 Â°C (cavity length of 2mm). Figure 3. Variation of the threshold current of BH laser chip on carriers as a function of aging time. The CoCs were stressed at 80 Â°C under 12.5 KA/Cm2 injection current density.

Poster

Delineating the roles of casein at the interface in enzymatic induced carbonate precipitation with highly spatial and temporal methods

Erin Dickey (Arizona State University)

Keywords:

Poster

TBD

Jannette Marti-Subirana (Arizona State University)

Keywords:

Poster

TBD

Nathan Miller (Arizona State University)

Keywords:

Poster

TBD

Jalynn Wells (Arizona State University)

Keywords:

Invited Talk

Biomolecular and materials structure determination by cryo-electron microscopy and microcrystal electron diffraction

Brent Nannenga (Arizona State University)

Keywords: Characterization, Fundamentals, Technology/Equipment; Biomolecular; Bio-(Inspired) Materials; Biomolecular; Biomolecular

High-resolution structure determination is critical for the fundamental understanding of biological, chemical, and materials systems. In this presentation, the application of cryo-electron microscopy (cryo-EM) methods for structure determination of difficult to study targets will be described. We make use of single particle cryo-EM methods to study the structures of protein-inorganic nanoparticle complexes at resolutions sufficient for the modeling and study of the protein structure and its interactions with the inorganic nanoparticles. Additionally, we make use of the recently developed method of microcrystal electron diffraction (MicroED) to rapidly determine high-resolution crystal structures of biological, chemical, and materials samples from very small amounts of sample. These samples contain microcrystals which are several orders of magnitude smaller than what is required for conventional X-ray diffraction methods, and here we will describe the MicroED method and its various applications for crystallographic structure determination.

Invited Talk

Nucleation Kinetics of Amorphous Carbonates in Confinement

Derk Joester (Northwestern)

Keywords:

Thermodynamic effects of stress on the crystal growth of apatite in aqueous environments

Alix Deymier (UConn Health), **Pierre Deymier** (University of Arizona), **Marat Latypov** (University of Arizona), **Krishna Muralidharan** (University of Arizona)

Keywords: Fundamentals, Growth, Modeling; Bulk; phosphates; Solution Growth; Nonlinear

Bone mineral deposition and growth is critical to maintaining healthy tissue mechanical function. It has been suggested that the application of mechanical stress via exercise promotes bone mineralization via cellular mechanotransduction and increased fluid transport through the collagen matrix. However, due to its complex composition and structure, bone mineral composition and crystallization is also expected to respond to stress. We have shown that interactions between bone mineral and surrounding fluids leads to ionic exchange between the substitutional solid mineral and the aqueous environment. Such substitutional systems have been shown by LarchÃ© and Cahn to exhibit stress-dependent compositional changes. We have additionally shown using molecular dynamics alongside synchrotron high-energy x-ray diffraction with in situ hydrostatic loading that these compositional changes have significant effect on bone mineral modulus. With this knowledge of interactions between bone mineral substitutions and loading, we hypothesized that bone mineral under applied stress would undergo compositional changes leading to modified mineral growth. To evaluate this, we developed an equilibrium thermodynamic model of bone apatite under stress in an aqueous solution based on the theory of thermochemical equilibrium of stressed solids. Inputting our previous experimental results into the model, indicated that that increasing uniaxial stress did indeed induce compositional variations. Specifically, a decrease in calcium and carbonate integration into the apatite solid. In addition, thanks to this substitutional effect, loading of the mineral crystal resulted in crystal growth. These results suggest, that due to the unique composition and structure of bone mineral, weight-bearing exercises can increase tissue mineralization via interactions between bone mineral and body fluid independent of cell and matrix behaviors, thus providing another mechanism by which exercise can improve bone health.

Biomimetic Control of Sequence-Defined Peptoids over Ag Nanocrystal Formation and Anisotropic Self-Assembly

Biao Jin (Pacific Northwest National Laboratory), **Md**. **Emtias Chowdhury** (Pacific Northwest National Laboratory), **Feng Yan** (Pacific Northwest National Laboratory), **Xin Qi** (University of Washington), **Jim Pfaendtner** (University of Washington), **James J De Yoreo** (Pacific Northwest National Laboratory), **Chunlong Chen** (Pacific Northwest National Laboratory)

Keywords: Characterization, Growth; 2D; Solution Growth

Simultaneously controlling the formation of metal nanoparticles and their anisotropic assembly into long-range ordered superstructures is crucial to the development of functional materials with various applications. While biomineralization directed by biomacromolecules (e.g. proteins) offers great inspiration for this purpose, current synthetic approaches remain a significant challenge. Herein, we report a peptoid-inspired strategy to direct the synthesis of ribbons consisting of ~2-3 nm Ag nanocrystals (NCs) by taking advantage of the well-controlled peptoid assembly driven by hydrophobic interactions, in which peptoid-peptoid and peptoid-Ag NC interactions can be manipulated by side chain chemistry. By examining the effects of peptoid side chain chemistries and varying reaction conditions as well as comparing the results to computational simulations, we reveal that the stronger interaction of peptoid-Ag NC than peptoid-peptoid contributes to the formation of the ultrasmall Ag NCs with a ~1.8 nm thick surface-adsorbed peptoid layer, and hydrophobic interactions drive their anisotropic assembly into the ribbons. Utilizing the ribbons as templates, we further synthesized bimetallic Pd@Ag NCs ribbons. This work presents a straightforward method for the synthesis of anisotropic 2D NC superstructures, and the developed approach here by taking advantage of tunable hydrophobic interactions offers tremendous opportunities for the design and preparation of functional NC superstructures with long-range ordering.

Multiphase silk assembly for two-dimensional composite

Chenyang Shi (Pacific Northwest National Laboratory), **Shuai Zhang** (University of Washington), **Marlo Zorman** (University of Washington), **Jim Pfaendtner** (University of Washington), **James De Yoreo** (Pacific Northwest National Laboratory)

Keywords: Characterization, Fundamentals, Growth; 2D; Biomolecule; Solution Growth; bio-device

Early insights into native silk fibroin (SF) architecture suggested that its unique structures and properties are determined by its multiscale assembly and the evolution of its secondary structure. Yet the pathways of assembly and the relationship to that evolution are poorly understood. Here we investigate SF self-assembly at using in situ AFM, photo-induced force microscopy. (PiFM), and molecular dynamics. To do so, we assemble the silk at the interface between water and highly ordered pyrolytic graphite (HOPG). We find that SF grows heteroepitaxially on HOPG into highly ordered, monolayer-thick 2D nanocrystals consisting of 1D lamellae that exhibit Î²-sheet secondary structure. Molecular dynamics simulations show that the lamellae strongly prefer the armchair orientation of HOPG and polar packing to form a bilayer. As the SF concentration increases, SF assembles into multi-layers via two pathways that can occur concomitantly. One is a non-classical pathway by which a disordered metastable film forms on top of the lamellae monolayer and gradually converts into the lamellae structure of SF Î²-sheet nanocrystals. The second is a classical layer-by-layer pathway by which new lamellae grow homoepitaxially on the underlying 2D lamellae nanocrystals without any evidence of an intermediate state. These new findings fill in the missing pieces of the puzzle showing how SF structure evolves at the liquid-solid interface and provides inspiration for the design of heterogeneous 2D SF composites.

Invited Talk

TBD

Kimberly Weirich (Clemson University)

Keywords:

TBD

Biologically Inspired Synthesis of Metal Oxide Particles with Varied Morphology and Orientation

Haitao Yu (University of California, Irvine), **David Kisailus** (University of California, Irvine)

Keywords: Growth; Thin Film; Silicon; Solution Growth; magnetite

Biological mineralization processes are widely recognized as a promising approach to synthesizing metal oxides under ambient conditions and near neutral pH, with precise control over their morphology, size, and crystallographic orientation. Nature provides valuable insights into these processes, as it often utilizes organic-mineral or organic-ion interactions to regulate biomineralization. By taking cues from nature, here, we control the growth of metal oxide particles on the surface of self-assembled monolayers (SAMs) with varying functional groups (such as â€“COOH, â€“CH3, and â€“OH). In order to investigate the nucleation and growth mechanism of metal oxides on the SAMs, as well as the interfacial energy for heterogeneous nucleation, we utilized SEM, XRD, TEM, and AFM to analyze the morphology, orientation, and nucleation rate.

Designed Interfaces Between Proteins and Inorganic Crystals for Templated Assembly and Co-Assembly

Sakshi Yadav Schmid (Pacific Northwest National Lab), **Amy Stegmann**, **Benjamin Helfrecht**, **Harley Pyles**, **Christopher Mundy**, **Shuai Zhang**, **David Baker**, **James de Yoreo**

Keywords: Characterization, Growth

Understanding and controlling the dynamic of protein assembly is essential to construct supramolecular structures and develop functional biomolecular materials. Recent advances in protein engineering have promoted accurate design of protein building blocks and protein-protein interfaces. However, although several hierarchical structures that exploit such designed interfaces and the anisotropic nature of protein building blocks have been developed, the thermodynamic and kinetic controls on the dynamics of assembly into supramolecular structures is still not properly understood. To investigate the emergence of order, we used high speed AFM (HS-AFM) to capture the assembly of protein nanorods into two-dimensional crystals at liquid-mineral interfaces. The protein nanorods have arrays of up to 54 carboxylate residues geometrically matched to the potassium ion (K+) sublattice on muscovite mica (001) and have been previously shown (Pyles et al. Nat. Let. 2019) to form two-dimensional liquid-crystal phases on the mica surface. Depending on the K+ ion concentration and the underlying mineral atomic structure, these nanorods can assemble into high density nematic or smectic phases or orientationally disordered phases. The emergence of order through active rotational degrees of freedom is then explored using a computational workflow, which combines artificial intelligence - based semantic segmentation and Fourier transform convolution - based instance segmentation to analyze the orientation and formation dynamics of protein nanorod domains. Additionally, to understand the underlying physical drivers of self-assembly, we performed an ensemble of Monte Carlo simulations for hard rods on a 2D lattice. By systematically varying the chemical potential, rod aspect ratio, and rod mobility across the simulation suite, we determined which conditions lead to nematic ordering, smectic ordering, and high-density disorder. By comparing the simulation results against experiments, we find that the hard rod model is largely sufficient to describe the experimentally observed behavior. Most importantly, we find that the rotational symmetry of the 2D potential and rod mobility are major factors in predicting the observed outcomes. This study is essential to demonstrate that proteinâ€"inorganic lattice interactions can be systematically programmed and are a steppingstone for designing proteinâ€"inorganic hybrid materials. Moreover, this study highlights the importance of high spatiotemporal resolution to visualize the rotational and translational motion and dynamics of nanorods during the emergence of order, the potential of artificial intelligence to analyze the emergence of this order, and significance of Monte Carlo simulations to determine the parameters that lead to this order. With the ensemble of experimental, artificial intelligence and theoretical techniques we can extract the underlying physical mechanisms of assembly.

Invited Talk

[CANCELLED]

Laurie Gower (University of Florida)

Keywords:

TBD

Tatumella morbirosei: A Study of Cyanophycin Synthetase and Cyanophycin

Alison Haymaker (Arizona State University), **Kyle Swain** (Arizona State University), **Itai Sharon** (McGill University), **Wyatt Blackson** (Arizona State University), **Sydney Parrish** (Arizona State University), **Stefan Tekel** (Arizona State University), **T. Martin Schmeing** (McGill University), **Brent L. Nannenga** (Arizona State University), **David R. Nielsen** (Arizona State University)

Keywords: Characterization; Sustainable Materials

Polymers produced by a living organism, or biopolymers, have many potential uses ranging from medicine, agriculture, cosmetics, nutrition, to bioplastics, making their research increasingly important.1 One such biopolymer is cyanophycin, produced by cyanophycin synthetases (CphAs) in cyanobacteria. Cyanophycin, or cyanophycin grana protein (CGP), is a polymer with an aspartic acid backbone and arginine as sidechains, and has shown to have promising elasticity for bioplastic use among many other uses.1 In a groundbreaking publication on CphA structure and activity, Sharon et. Al. solved the CphA structure from Tatumella morbirosei, which is mostly known as a contributory factor in Pink Disease in pineapples.2,3. In collaboration with Sharon et. Al. we further characterize CphA from Tatumella morbirosei (tmCphA) and the resulting CGP produced. 1. Du, J., Li, L., & Zhou, S. (2019). Microbial production of cyanophycin: From enzymes to biopolymers. Biotechnology Advances, 37(7). https://doi.org/10.1016/j.biotechadv.2019.05.006 2. Sharon, I., Haque, A. S., Grogg, M., Lahiri, I., Seebach, D., Leschziner, A. E., Hilvert, D., & Schmeing, T. M. (2021). Structures and function of the amino acid polymerase cyanophycin synthetase. Nature Chemical Biology, 17(10), 1101â€“1110. https://doi.org/10.1038/s41589-021-00854-y 3. Brady, C. L., Venter, S. N., Cleenwerck, I., Vandemeulebroecke, K., De Vos, P., & Coutinho, T. A. (2010). Transfer of pantoea citrea, Pantoea punctata and Pantoea terrea to the genus Tatumella emend. as Tatumella citrea comb. Nov., Tatumella punctata comb. nov. and Tatumella Terrea Comb. nov. and description of Tatumella Morbirosei sp. nov.. International Journal of Systematic and Evolutionary Microbiology, 60(3), 484â€“494. https://doi.org/10.1099/ijs.0.012070-0

SINGLE PARTICLE CRYO-EM STRUCTURE OF FERRITIN BIOMINERALIZATION SHOWING THE PROTEIN-NANOPARTICLE COMPLEX

Sagnik Sen (Arizona State University)

Keywords: Characterization; Oxides; Solution Growth

Ferritin is a ubiquitous, globular protein that can assemble into a highly symmetric nanocage which mineralizes iron nanoparticles in its inner shell. It is the primary iron storage protein in organisms and is responsible for iron homeostasis. Elucidating the molecular interactions driving the mineralization will help better understand the nucleation and growth and also can help further engineer them for various bio-material applications. Single particle cryogenic electron microscopy (Cryo-EM) is a powerful structural biology tool which images proteins in their native functional state and has previously been used to obtain an atomic resolution model of Apoferritin. In our previous work demonstrating Cryo-EM as a promising tool for studying biomineralization, two different cases (including Ferritin) were analyzed structurally. We obtained a low resolution map in case of Ferritin and thus not much structural information at the mineralization interface could be obtained. In our current study we use Cryo-EM data processing including nanoparticle masking, to observe the biomineral formation in Human Light Chain Ferritin (HuLF). We present a 4 Ã… structure of the Ferritin-Iron nanoparticle complex. This resolution allowed us to fit the model of Apo-HuLF (PDB 2FFX) to the map we obtained. The amino acid residues at the protein-nanoparticle interface can be observed and provide information regarding interacting molecules responsible for the mineralization. Previous X- ray crystallography studies have shown glutamic acid residues on the inner surface of the light chain Ferritin shell to be responsible for the formation of the initial iron nucleation cluster. Our model shows the formed iron nanoparticle to be centered around the above mentioned residues. A larger Cryo-EM data set has also been collected and is being processed to get better resolution maps. Furthermore this study also sets the template for structural analysis of more protein mediated biomineralization cases which can lead to better rational design of bioengineered nanomaterials.

Delineating the Roles of Casein at the Interface in Enzyme Induced Carbonate Precipitation (EICP) with Highly-Resolved Spatial and Temporal Methods

Logan Tsosie (Arizona State University), **Edward Kavazanjian** (Arizona State University), **Jong Seto** (Arizona State University)

Keywords: Characterization, Growth; Bulk; Silica; Biological; Twisted Crystal; Sustainable Materials

Current state-of-art methods to mineralize in situ silica sands for geotechnical purposes include the use of biological small molecules and bacterial cells to induce carbonate precipitation. Specifically, my work will examine the roles of organic molecules in the modified protocol of an enzymatic inducement of carbonate precipitation (EICP), specifically, how casein molecules at the interface of silica sand grains aid in the formation of the carbonate mineralization front and affect nucleation and crystal growth of carbonate minerals. With advanced methods like scanning electron microscopy and X-ray micro-tomography, we can observe at high spatial and temporal resolutions how casein molecules are co-localized to silica sand surfaces and boundaries to initiate carbonate nucleation and their roles in affecting subsequence carbonate crystal growth. By perturbing the solubility of casein in solution, we can modulate the initial mineralization events to further optimize the bonding between silica sand grains and eventually, the elastic moduli of the resulting mineralized material. We demonstrate that this method can be tuned for specific sand properties and can be optimized for a variety of geotechnical applications.

Invited Talk

Bulk Crystal Growth and Opto-electronic Characterization of Î²-Ga2O3

John McCloy (Washington State University), **Benjamin Dutton** (Washington State University), **Jani Jesenovec** (Washington State University), **Marc Weber** (Washington State University), **Matt McCluskey** (Washington State University)

Keywords: Characterization, Growth; Bulk; Oxides; Melt Growth; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

For more than 25 years, the Institute of Materials Research (IMR) â€“ formerly the Center for Materials Research â€“ at Washington State University has worked to develop II-VI and other crystal materials for applications ranging from lasers to detectors to solar cells. In this talk, we will reintroduce the IMR and the current Crystals And Semi-Conductors (CASC) group its current research portfolio. We will discuss a specific area of current research: gallium oxide crystals, where we have performed >70 separate growths to date. Much excitement has surrounded the accelerating development of Î²-Ga2O3 for electronics due to its ultrawide band gap, high breakdown voltage, compatibility with many dopants, and comparative ease of producing large substrates via melt-growth techniques. Our research has focused on growth and characterization of Czochralski (CZ) and vertical gradient freeze (VGF) single crystals of Î²-Ga2O3 with various dopants, including donors (Zr, Hf, Cr), acceptors (Mg, Zn, Fe, Ni, Cu, Mn), and alloying elements (Al, Sc, In). We find in general that doping in CZ and VGF materials can be different and sometimes non-uniform due to the interaction with crucible material (Ir), selective evaporation, and thermal profile. We have also explored the creation and identification of gallium vacancies (VGa) through annealing, by using positron annihilation spectroscopy (PAS), hydrogenated Fourier Transform Infrared (FTIR) spectroscopy, and electrical measurements. Insights from our work to date are offered, in terms of their applicability to devices.

Experience-based Feedforward control of Czochralski growth process using data processing.

Jan Kovar (CRYTUR, spol. s r.o.), **Martin Klejch** (CRYTUR, spol. s r.o.), **Jan Polak** (CRYTUR, spol. s r.o.), **Jindrich Houzvicka** (CRYTUR, spol. s r.o.)

Keywords: Growth, Modeling; Bulk; Oxides; Melt Growth; Scintillator; Energy Materials, Optical Materials, Scintillator Materials

Experience-based Feedforward control of Czochralski growth process using data processing. Jan KovÃ¡Å™, Martin Klejch, Jan PolÃ¡k, and JindÅ™ich HouÅ¾viÄ□ka CRYTUR, spol. s r.o., Turnov, Czech Republic Presenting author: kovar@crytur.cz For the well known Czochralski growth process there is nonexisting steady state operating point [1]. As solution, many types of feedforward control methods were proposed [1,2]. These methods need detailed model of growth process. For mass production it is advisable to use experience based model. For this type it is necessary to log crucial parameters of growth process. That means, to record parameters of growth process every few seconds. The mount of data is over one million values for one parameter in one growth process. For good fitting, more then 10 records of growth process is required. As solution automatized data record and automatized computation of forecast function is necessary. For our model we consider one type of crystal growth with the same growth parameters. Our model material is Nd:YAG. Time dependent function of heater power for each crystal is similar to the next one. This is a crucial feature, which enables to build Feedforward estimate for the next crystal. The goal is to find time dependent function which predicts the necessary heater power. This heater power of growth cycle was recorded for ten crystals (training the model). This data has been represented in 3 dimension and fitted by polynomial surface (Eq.1), Where: S-surface function, t â€“ time, i â€“ crystal number, m,n-polynomial degree. S=a_(m,n) t^m i^n+a_(m,n-1) t^m i^(n-1)+a_(m-1,n) t^(m-1) i^n+a_(m-1,n-1) t^(m-1) i^(n-1) ã€–â€¦+aã€—_0,1 i+a_00 (Eq.1) For the calculation this function surface fitting in least square method was used. Feedforward time dependent function we give as extrapolation this surface for crystal n=11. P_p=a_(m,n) t^m ã€–11ã€—^n+a_(m,n-1) t^m ã€–11ã€—^(n-1)+a_(m-1,n) t^(m-1) ã€–11ã€—^n+a_(m-1,n-1) t^(m-1) ã€–11ã€—^(n-1) ã€–â€¦+aã€—_0,1 11+a_00 (Eq.2) Heater power is calculated by: P_C=P_0+P_PID+P_p (Eq. 3) Quality of predication can be evaluated by maximum slope of difference between prediction and reality. Its means that PID regulator is closer to steady state. This methods was implemented in new Crytur growing facility. References [1], M. Neubert, J. Winkler, Nonlinear model-based control of the Czochralski process IV: Feedforward control and its interpretation from the crystal grower×³s view,Journal of Crystal Growth,Volume 404,2014, Pages 210-222, ISSN 0022-0248,. [2] Michael A. Gevelber, Michael J. Wargo, George Stephanopoulos,Advanced control design considerations for the Czochralski process,Journal of Crystal Growth,Volume 85, Issues 1â€“2,1987,Pages 256-263,ISSN 0022-0248, Acknowledgments: This work is supported by the project FW01010038

Growth of large diameter yttrium aluminium garnet crystals by Czochralski method

Jan Polak (Crytur spol. s. r. o.), **Jindrich Houzvicka** (Crytur spol. s. r. o.)

Keywords: Growth; Bulk; Oxides; Melt Growth; Scintillator; Optical Materials, Scintillator Materials

Yttrium-aluminium garnet (YAG, Y3Al5O12) is well-known oxide material for optical applications and is widely used as a host material mainly for solid-state lasers and scintilators. YAG exhibits good mechanical properties, chemical and thermal stability and wide transparency range. It is a suitable host material for many dopant ions and it can be produced easily in a commercial scale. YAG single-crystals are mainly produced by Czochralski method (CZM). Production of YAG has been utilized for decades, however, there are still new challenges in this technology. One of them is the production of YAG crystals with a large diameter and high optical quality. This presentation introduces state-of-the-art undoped, Ce3+, Yb3+ and Nd3+ doped YAG crystals, manufactured by CZM in the Crytur company. Numeric modelling of thermal field and maximum utilization of the melt contained within the crucible allowed to enlarge the diameter up to 120 mm and weight 10 kg. Precise control of pulling rate and rotation the crystals was necessary to keep the flat growth interface. Different crystal orientations <111> and <100> were used according to the final application. Core-free and minimized strain was achieved through temperature regime regulation and by defining the position of the minimum temperature isotherm in the crucible using the temperature gradient in the direction of the top rim of the crucible. Ce:YAG is a fast scintillator preferred for electron microscopy, beta and X-ray counting, as well as for electron and X-ray imaging screens. When exposed to electrons, X-ray, UV or blue light Ce:YAG emits yellow light with maximum at 550 nm. Standard imaging screens previously manufactured had diameter max 50 mm. Nowadays CZM allows to produce imaging screens diameter up to 100 mm and thickness down to 0,1 mm. Growing condition were optimized to reduce concentration strips caused by unfavorable Ce3+ segregation coefficient. Yb:YAG is a promising laser material with broad absorption bandwidth. It generates 1030 nm laser output pumped at 940 nm. Yb:YAG is usually manufactured in the form of rods or slabs which are prefered in high power-applications. Yb3+ ions have favourable segregation coefficient equals near 1. Modified CZM technique enables to produce uniformly doped crystals for slabs with core-free diameter more than 80 mm. Nd:YAG is one of the most common laser material widely used in medicine, military and welding-cutting. Typically emits infrared light with a wavelength 1064 nm. Increasing the diameter of the crystal led to a deterioration of the optical homogeneity and stabilization of growth interface was needed. Acknowledgments: This work is supported by the project FW01010038 by Technology Agency of the Czech Republic.

Bulk Crystal Growth of $Yb_3Ga_5O_{12}$ and $GdLiF_4$ for Adiabatic Demagnetization Refrigeration Devices

Adam Lindsey (Northrop Grumman SYNOPTICS), **Kelvin Chang** (Northrop Grumman SYNOPTICS), **Greg Foundos** (Northrop Grumman SYNOPTICS), **Chase Scott** (Northrop Grumman SYNOPTICS), **Kevin Stevens** (Northrop Grumman SYNOPTICS), **Allen Brady** (Northrop Grumman SYNOPTICS)

Keywords: Growth; Fluorides, Oxides; Melt Growth; Adiabatic Demagnetization Refrigeration

The growth of bulk single crystals of $Yb_3Ga_5O_{12}$ (YbGG) and $GdLiF_4$ (GLF) and has received attention for adiabatic demagnetization refrigeration (ADR) devices to reach temperatures at and below 1 K. Two key metrics for an ADRâ€™s performance include volumetric density of magnetic ions and thermal conductivity. Bulk single crystals of ADR materials therefore offer inherent advantages as they have a higher density and thermal conductivity over their polycrystalline counterparts. We used our expertise in growing other rare earth gallium garnets to demonstrate bulk crystal growth of YbGG 35mm diameter up to 55mm long. GLF is isostructural to the more developed material, $YLiF_4$ Â¬(YLF), but is more challenging owing to its highly incongruently melting behavior. We overcame this challenge and have demonstrated bulk crystal growth of GLF 25mm diameter up to 120mm long. These single crystals are believed to offer advantages over components used in existing ADR technology.

Invited Talk

Crystal growth and characterization of large Ca0.582Sr0.418F2 single crystal by Czochralski method using cone die

Kazuya Takahashi (Fukuda Crystal Laboratory Co., Ltd.), **Marilou Cadatal-Raduban** (Massey University), **Nobuhiko Sarukura** (Osaka University), **Toru Kawamata** (Institute for Materials Research, Tohoku University), **Kazumasa Sugiyama** (Tohoku University), **Tsuguo Fukuda** (Fukuda Crystal Laboratory Co.)

Keywords: Growth; Bulk; Fluoride; Melt Growth; Optical Materials

Calcium fluoride (CaF2) is mainly used as an optical material in the vacuum ultraviolet (VUV) region, which spans the wavelength range from 200 nm down to 100 nm, because of its excellent transparency. CaF2 is particularly useful in photolithography using ArF lasers at 190 nm because it is optically durable to withstand long exposures to high-energy laser light. In recent years, there has been an increasing demand for more durable optical materials as lasers have become more powerful. Therefore, CaF2 and other new materials with higher durability and quality are required. In addition, at least 2-inch diameter large crystals are needed for practical applications. However, pure CaF2 has several limitations that need to be overcome, such as high cleavage, F defects, structural phase transition at high temperatures [1], and birefringence in the short wavelength region. Mixed crystals have been proposed to address the problem of birefringence [2]. Here, we report the growth of large Ca0.582Sr0.418F2 single crystal with a maximum diameter of 4 inches. The Ca0.582Sr0.418F2 crystal was grown by the Czochralski (CZ) method using a resistance-heated CZ furnace and a conical graphite die that was placed inside the crucible for melting the raw material. During crystal growth, the outer crucible was raised to allow the melt to penetrate through the hole into the inner die. The conical graphite die provided a heat shield that brought about a lower temperature above the melt, effectively preventing the seed crystal from melting. By using a slanted opening at the die, the diameter of the growing crystal was controlled by adjusting the height of the melt in the die. The raw materials used consisted of polycrystalline powders with a purity of 99.99% (4N). CaF2 single crystal with (100) and (111) orientation was used as seed crystal. The Ca0.582Sr0.418F2 crystal was grown in Ar atmosphere. The obtained ingot was confirmed to be a single crystal by measuring Laue reflection patterns at several different positions. Characterization showed a small compositional variation between the starting composition and the grown crystal, along with a high degree of homogeneity. Further characterization confirmed that the single crystals have excellent optical properties. The transmittance at 200 nm wavelength is more than 99%, making it highly transparent in the VUV region. There were no noticeable internal bubbles, cracks, or light scatterers. References: [1] P.Fossati, et.al, Frontiers in chemistry 9 (2021) 723507. [2] J.H.Burnett, et.al, Phys. Rev. B 64 (2002) 241102.

Invited Talk

Solution Phase Diagram of Lead Zirconate Titanate (PZT) in a High Temperature Solution

Vincent Fratello (Quest Integrated, LLC), **Song Won Ko** (Quest Integrated, LLC)

Keywords: Growth; Bulk; Oxides; Flux Growth, Solution Growth; Ferroelectric, Piezoelectric; Ultrasound

Lead zirconate titanate (PZT) of composition Pb(ZrxTi1ï€x)O3 is the dominant piezoelectric material in non-destructive testing because of its high efficiency and high-power capability. PZT is a solid solution perovskite between lead zirconate (PZ) and lead titanate (PT), but PZT is non-congruent, meaning it cannot be grown from a melt of the same composition. The crystal structure of lead titanate is tetragonal and that of lead zirconate is rhombohedral. The solid solutions of PZ-doped PT and PT-doped PZ have the structure of the host until the compositions approach the center of the phase diagram. At the center of the phase diagram, these structures become unstable with monoclinic structures appearing. This region is called the morphotropic phase boundary (MPB) and is centered at x ï‚» 0.52 atoms per formula unit of Zr. Past phase diagram work has shown this compositional range to be unstable and subject to phase separation. To grow PZT crystals in the MPB region, it is first necessary to understand the solution phase diagram of PZT. Liquidus-solidus compositional pair data from a variety of innovative flux systems over a range of temperatures have been taken and did not fit the previous phase diagram results from the literature. A set of equations to model the thermodynamic equilibria have been developed and a complete free energy derivation was performed to a closed form for the growth of a solid solution from a liquid solution that also contains a solvent not incorporated into the crystal. This model was fit to the data with good agreement. The results are more than just a theoretical exercise. When fit to the growth data already taken, these equations allow the determination of important thermodynamic parameters, accurate construction of a phase diagram and plotting of free energy curves that elucidate issues of phase separation in PZT and how it can be avoided. As a result, compositional equilibrium, optimum flux composition and growth conditions, and crystal growth have been achieved over a wide range of crystal compositions without phase separation including the desired equimolar composition range.

Vertical gradient freeze growth of 8 inch diameter semiconducting GaAs

Wei Gao (AXT Inc.), **Weiguo Liu** (AXT Inc.), **Yuanli Wang** (Beijing Tongmei Xtal Technology Inc.), **Shuhui Zhang** (Beijing Tongmei Xtal Technology Inc.), **Tim Bettles** (AXT Inc.), **Rajaram Shetty** (AXT Inc.), **Morris Young** (AXT Inc.)

Keywords: Growth, Technology/Equipment; Bulk; III-Vs (Traditional); Melt Growth; III-V direct band gap semiconductor; Energy Materials, LEDs, VCSELs, micro-LEDs, Sustainable Materials

There is an increasing demand for GaAs wafers for applications such as LED displays, micro LEDs and VCSELs in AR/VR and automotive applications and for RF electronics for mobile and consumer applications. In order to achieve the higher volumes demanded from the new applications at lower costs, increasing the wafer size to 8â€□ diameter from currently available smaller diameters such as 4â€□/6â€□ could be beneficial. Producing 8â€□ diameter GaAs crystals however, poses several challenges due to the properties of GaAs such as poor thermal conductivity in the solid, weaker bonding resulting in a large number of defects and so the need to maintain appropriate heat transfer conditions to achieve single crystal growth with low enough defect densities required for the above applications. We present a process and initial results achieved for 8â€□ diameter semiconducting GaAs crystals grown by a vertical gradient freeze technique. By an appropriate choice of furnace system hardware, temperature distribution and growth conditions, 8â€□ diameter GaAs crystals have been produced with properties similar to the smaller diameter crystals. Results will be presented in terms of crystal quality such as dislocation density and electrical properties.

Controlling Morphology of NiSb Needles in InSb through Low Temperature Gradient Horizontal Gradient Freeze

Jani Jesenovec (BAE Systems), **Kevin Zawilski** (BAE Systems), **Stephan Meschter** (BAE Systems), **Sambit Saha** (BAE Systems), **Peter Alison** (BAE Systems), **Peter Schunemann** (BAE Systems)

Keywords: Growth; Bulk; III-Vs (Traditional); Melt Growth; Narrow Semiconductor; Energy Materials, Optical Materials

InSb has been historically grown as poly or single crystals for a variety of electro-optical applications. When NiSb is added to InSb, NiSb needles form in the InSb matrix due to a eutectic phase diagram. The size and morphology of the NiSb needles in the InSb can be manipulated and used in devices that have a tunable magnetoresistance. InSb has a zincblende (F43 m) structure and the NiSb needles are in the hexagonal wurtzite structure. In this work, InSb alloyed with 1.8 wt.% NiSb was grown in a Horizontal Gradient Freeze (HGF) furnace with low thermal gradients andgrowth rates ranging from as low as 0.05 cm h-1 to 1 cm h-1. Literature reported growth rates in the range of 0.5 â€“ 6 cm h-1 in previous work on this system. Lower growth rates resulted in larger InSb grains, and when the growth rate was increased to 1 cm h-1, InSb grain size decreased and the NiSb needle morphology changed. One obstacle encountered during the growth process was the formation of surface slag which has been known to contaminate growth and act as nucleation centers. In this case, the surface slag was identified as indium oxide formation, and was remedied through etching of precursor material. Device performance varied depending on the density and alignment of these NiSb needles, as well as the resistivity of the single crystal matrix. The density of NiSb needles in the InSb matrix & the needle length were shown to be predominantly dependent on growth rate, which was subsequently optimized for the final magnetoresistor application. These experiments produced bulk crystals with needles aligned along the growth direction, with properties that are promising for modern magnetoresistor applications. Undoped InSb crystals were also grown at 0.05 cm h-1 via HGF and demonstrated good IR transmission at room temperature.

Poster

Magnetization - induced spin current flip in (4R)FeO3 single crystal (R- Rare-earth)

Ramki Chakaravarthy (Saveetha Engineering College), **Tarak Bachagha**, **Wencheng Fan**, **Shixun Cao**, **Wei Ren**

Keywords: Fundamentals; Bulk; Oxides; Melt Growth; Spintronics; Quantum Materials

Recently, a class of oxide materials which are characterized using â€˜nâ€™ number of elements (i.e., four or more) in one lattice site and they are structurally crystallized in a single phase form. Here, we successfully grown such a single crystal (4R)FeO3 which is occupied by four different rare-earth elements (Sm, Er, Gd, Eu) in A-site while B-site has a single transition metal iron (Fe) ion using optical floating zone technique. (4R)FeO3 is a well-defined single crystal with 5.2 cm in length was grown in oxygen atmosphere and the recorded powder X-ray diffraction confirmed the single-phase orthorhombic (Pbnm) perovskite structure. In this compound, we observed an intriguing magnetic property which emerge from the non-zero electron spin ground state interaction between R 3+ and Fe 3+ that leads to a different kind of transitions like type-I spin switching (Sm 3+ -Fe 3+ -Er 3+) in the ZFC curve along a-axis at 22 K for 50 Oe of field, at the same time type-II spin switching (Er 3+ -Fe 3+) occurs at 101 K for 20 Oe and 67 K for 10 Oe along with the spin oscillation of Gd 3+ ion. The strong mutual controllability between Er 3+ and Gd 3+ spins suppressed the magnetization drop (Er 3+) at high temperature above 30 Oe of applied field. The spin reorientation transition temperature occurs between 98 and 128 K (Î“ 4 â†’ Î“ 2) and this could be the highest spin reorientation transition with four and above rare-earth elements in A-site. The large coercive field with very small magnetization at 10 K and electrical switching at 20 K in M- H loop proved that the material is highly intergrated with the magnetic flux density and this kind of material can be utilized in the field of antiferromagnet spintronics.

Poster

Influence of Eu 3+ doped on the spin reorientation in the imperfect antiferromagnetic system of Sm 1-x Eu x FeO 3 (x = 0.25, 0.5 and 0.75) single crystals

Ramki Chakaravarthy (Saveetha Engineering College), **Tarak Bachagha**, **Arnab Pal**, **Shixun Cao**, **Wei Ren**

Keywords: Growth; Bulk; Oxides; Melt Growth; Spintronics; Quantum Materials

A key challenging task in physical materials is to control or tuning the spin reorientation transition from low to room to high temperature by incorporating an appropriate dopant in A or B sites of perovskite oxides. In RFeO 3 materials (R-rare-earth), SmFeO 3 is the only material having the spin reorientation transition above room temperature and also shows other exciting physical observation whereas EuFeO 3 has no such physical property because the total spin angular momentum of Eu has J = 0 and the corresponding exchange interaction with the Fe ions are weak or absent. This work will address the activation of interaction between Eu and Fe ions via Sm ions and the influence of Eu 3+ on Fe 3+ and Sm 3+ has been investigated by growing a series of orthorhombic single crystals, Sm 1-x Eu x FeO 3 (x = 0.25, 0.5 and 0.75) using optical floating zone method. The magnetic measurement shows that the magnetism arises from the imperfectly aligned Eu domain, a non-equivalent sublattice in the antiferromagnetic structure. The increase in the total magnetization arises from the parallel spin polarizing effect of Eu 3+ to the net iron moment against the anistropy exchange interaction of Sm 3+ -Fe 3+ and that could be the reason for the absence of temperature compensation and spin switching transition in the material. The change in free energy between the Sm 3+ -Eu 3+ shift the spin reorientation transition (SRT) temperature from 65-130 to 220-275 to 350-395 K with respect to the ratio of Eu 3+ ions. And the change in the magnitude in the cross over between a and c- axis might be due to the inelastic relaxations of magneto-elastic origin. The M-H signal shows the unsaturated Eu domains in the antiferromagnetic exchange up to 3 T in the SRT region and it is expected to be aligning like monodomanization at high magnetic field strength. In summary, the grown series single crystal of Eu doped SmFeO 3 has been utilized for the spin based electronic system at room temperature through spin reorientation transition.

Poster

Nucleation parameters, thermal and mechanical behavior of nonlinear optical potassium hydrogen oxalate trihydroxyborate single crystal

Ajisha D S (Vellore Institute of Technology, Vellore), **Ezhil Vizhi R**

Keywords: Characterization, Growth; Bulk; Solution Growth; Nonlinear; Optical Materials

A single crystal of potassium hydrogen oxalate trihydroxyborate (KHOB) was grown by adopting slow cooling method. The presence of boron and oxalate in the grown material was confirmed with the help of single-crystal XRD. With the help of the classical theory of nucleation, the various nucleation parameters of the grown crystal were calculated for optimizing the growth condition. The mechanical behavior of the material was analyzed with the help of the Vickers microhardness analysis. The material was exhibiting the reverse indentation effect and various mechanical parameters were calculated for analyzing its mechanical behavior. Meyer's index number of the material was 2.1 which indicate that the material belongs to the soft material category. The material was thermally stable up to 115Â°C and the different decomposition stages of the grown crystal were analyzed with the help of the thermogravimetric analysis. Kurtz-Perry method was adopted to measure the SHG efficiency of the grown material and was found to be 0.34 times that of KDP material, which indicates the NLO application of the grown material. Keywords: Slow cooling technique, Nucleation kinetics, single crystal XRD, Nonlinear optical material References: 1. Ajisha D. S., R. Ezhil Vizhi, Structural, dielectric and nonlinear properties of potassium hydrogen oxalate-trihydroxy boron (KHC2O4 B(OH)3) single-crystal, J. Solid State Chem. 293 (2021) 121642 2. Bhat, H. L. (2014) Introduction to crystal growth: principles and practice. CRC Press 3. P.N. Prasad, D.J. Williams, Introduction to nonlinear optical effects in organic molecules and polymers, Wiley, New York, 1991

Poster

Optical characteristics of multifunctional heavy metal based multifunctional materials

Amalthea Trobasre (University of Maryland Baltimore County), **Meghan Brandt** (University of Maryland Baltimore County), **Ching Hua Su** (NASA Marshall Space Flight Center, AL), **Leslie Scheurer** (University of Maryland Baltimore County), **Bradley Arnold** (University of Maryland Baltimore County), **Fow-Sen Choa** (University of Maryland Baltimore County), **Narasimha Prasad** (NASA Langley Research Center), **Brian Cullum** (University of Maryland Baltimore County), **N**. **B**. **Singh** (University of Maryland Baltimore County)

Keywords: Devices, Growth; PVT; Nonlinear, Scintillator; Optical Materials, Scintillator Materials

Heavy metal based multifunctional materials have enormous potential for variety of electronic, optical and radiological applications due to large bandgap and low damage possibility for space applications. We have developed and fabricated binary and ternary mercury, thallium and lead based variety of imaging, optical and radiological sensing and laser developments. These materials have been extensively used in developing acousto-optic, delay lines, high power MWIR and LWIR lasers, and radiation sensors. Device quality crystals were grown by Physical vapor transport method and Bridgman growth method. Detailed studies using near IR and MWIR radiations for emission characteristics show very distinct difference at room and cryogenically cooled temperatures. We have used near-IR radiations to study mercurous chloride (Hg_2Cl_2), mercurous bromide (Hg_2Br_2), thallium gallium selenide ($TlGaSe_2$) and thallium arsenic selenide (Tl_3AsSe_3) crystals at room temperature and at cryogenic temperatures to evaluate their suitability for space applications.

Invited Talk

Synthesis and Characterization of Novel Metal Thiophosphate Materials

Michael Susner (Air Force Research Laboratory), **Rahul Rao** (Air Force Research Laboratory), **Enam Chowdhury** (The Ohio state University), **Bing Lv** (UT Dallas)

Keywords: Characterization, Growth; 2D; Novel; Flux Growth, Melt Growth, PVT; Ferroelectric, Nonlinear; Optical Materials

Recently, research in layered materials has rapidly expanded due to their potential applications in photonics and optoelectronics. Here, we detail the optical properties of members of the 2D and 3D metal thiophosphate materials. Sn2P2S6 is a well-known 3D ferroelectric material with a TC of 337 K; CuInP2S6 is a similarly well-known 2D ferrielectric with a TC of 315 K. Our efforts have revealed important information regarding the nature of their multiple ferroelectric potential wells. We will also discuss second harmonic generation in more exotic AgScP2S6 and CuScP2S6 and the optical properties exhibited by these new materials. These include a giant two photon absorption (TPA) process and its saturation in AgScP2S6 and structure-property examination by traditional optical, thermal, and diffractive techniques.

Invited Talk

Low-Background Crystals for Rare Event Searches in Nuclear and High Energy Physics

Joshua Tower (Radiation Monitoring Devices, Inc.), **Guido Ciampi** (Radiation Monitoring Devices, Inc.), **Yaroslav Ogorodnik** (Radiation Monitoring Devices, Inc.), **Huicong Hong** (Radiation Monitoring Devices, Inc.), **Lindley Winslow** (Massachusetts Institute of Technology), **Joseph Formaggio** (Massachusetts Institute of Technology), **Aldo Ianni** (INFN Laboratori Nazionali del Gran Sasso), **Michael R. Squillante** (Radiation Monitoring Devices, Inc.)

Keywords: Growth; Bulk; Oxides; Melt Growth; bolometer, Scintillator; bolometer, superconductor, Scintillator Materials

Crystals with extremely low radioactivity background are needed as detectors for various physics research experiments that probe some of the most fundamental mysteries of the universe, such as the nature of the neutrino or of dark matter. Because the interactions to be investigated are rare and sometimes faint, extreme measures are taken to reduce all background signals and other noise. Experiments are situated in deep underground laboratories to reduce cosmic ray interference. Large arrays of detector crystals, tens to hundreds of kilograms, are needed to produce sufficient count rates for statistical significance. Additional background reduction can be achieved by experimental designs that provide a veto for some backgrounds or by advanced detectors that can provide particle discrimination. This talk will review RMDâ€™s work in developing several low-background crystals that are used for rare event searches in nuclear and high energy physics. While the crystals for various applications are quite different, there is a lot of commonality in the processes used to produce them. The crucial processes must maintain or improve the material purity at all stages. These include purification of the raw materials, synthesis and crystal growth, and post-growth fabrication. We will discuss the methods and precautions required to achieve suitable low background crystals. We will present three examples of low-background crystals used for different physics applications. Lithium molybdate (Li2MoO4) is a scintillating bolometer used in the neutrinoless double-beta decay search. Sodium iodide (NaI) is a room temperature scintillator used for dark matter search. Zinc and aluminum crystals are used as superconducting bolometers for neutrino scattering experiments. We will discuss each application and present examples of crystal performance. This work has been supported by the US Department of Energy SBIR grants No. DE-SC0015200, DEâ€□SC0023588, and DE-SC0013760.

Invited Talk

Hydrothermal Growth of Magnetically Frustrated Crystals: Lanthanide Stannate Pyrochlores as a Prototype

Joseph Kolis (Clemson University), **Matthew Powell** (Clemson University)

Keywords: Growth; Bulk; Oxides; Solution Growth; magnetic; Quantum Materials

Single crystals containing magnetically frustration are a rich source of nonclassical physical properties. They can act as spin liquids, spin ices and many other unusual states. These can serve as gateways to quantum materials by generating massively degenerate ground states that can only be explained by nonclassical quantum states. Typically such frustrated systems require trigonal crystal lattice sites occupied by magnetically active ions. In this case antiferromagnetic ordering generates highly frustrated systems that cannot resolve their magnetic coupling by classical routes. This can generate residual zero point entropy leading to massively degenerate ground states. One important test bed system for frustrated magnetism is the pyrochlore lattice with the formula A2B2O7 in the cubic space group Fd3m. Both the A and B sites occupy crystallographic trigonal sites and both sites possess a tetrahedral relationship with the other similar metal ions. These symmetry relationships generate a 3D frustrated structure. In frustrated magnetic systems typically a trivalent lanthanide ion occupies the A site and a magnetically silent tetravalent ion (Ti, Zr, Sn, etc) occupies the B site. A classical problem related to the crystal growth of these compounds is sample quality. As refractory oxides, the traditional synthesis and crystal growth techniques require high temperatures. This creates two problems that are quite common and endemic to the pyrochlores. One is oxide lattice defects and the other is A/B site disorder. Both issues often occur in that same crystals and have a significant impact on the study of physical properties. A hydrothermal approach can be applied to this problem. The relatively low crystal growth temperatures and pressures (600-700ËšC/200MPa) greatly minimize nonstoichiometry, lattice defects and A/B site disorder. The reduction of these pervasive imperfections significantly increases the quality of the observed physical property data. This talk will focus on the lanthanide stannates Ln2Sn2O7 as a prototype test bed of these systems. The stannates are among the few building blocks that can stabilize the pyrochlore structure type for all the lanthanides and they serve as an excellent proving ground for a wide range of physical properties. The synthesis and crystal growth of the lanthanide stannates will be discussed, along with a discussion of some of the physical properties that result from the frustrated magnetic states of these low defect crystals.

Invited Talk

Optical emission characteristics of PVT grown doped ZnSe crystals in near IR wavelength region

Narsingh Singh (University of Maryland Baltimore County), **Ching Hua Su** (NASA Marshall Space Flight Center), **Bradley Arnold** (University of Maryland Baltimore County), **Meghan Brandt** (University of Maryland Baltimore County), **Eric Bowman** (University of Maryland Baltimore County), **Leslie Scheurer** (University of Maryland Baltimore County), **Fow-Sen Choa** (University of Maryland Baltimore County), **Brian Cullum** (University of Maryland Baltimore County)

Keywords: Characterization, Devices, Technology/Equipment; PVT; Nonlinear; Optical Materials

Pure and doped zinc selenide (ZnSe) crystals have been used for variety of devices in the bulk crystal and transparent coating applications. Because of this reason ZnSe and ZnS have been designated as multifunctional materials for optical and electronic devices. The doping can cause significant changes in the fluid flow and hence convection during crystal growth by the physical vapor transport method used in growing ZnSe crystals. Based on the birefringence and, reflectance (all optical) measurements) and comparison with emission characteristics it is clear that doping induced point defects in Cr-ZnSe and Fe-ZnSe crystals. It was observed that the overall emission using small wavelength and longer wavelength source indicated good emission characteristics. There was slight effect of local population of defects in the peak characteristics of the emission. There was significant effect of doping on the electrical characteristics such as resistivity, capacitance and bandgap changed for the better applications. For example, resistivity and also the bandgap increased indication that doped materials have great potential for high voltage applications compared to pure ZnSe crystals.

Invited Talk

Design and Discovery of Superior Nonlinear Optical Crystals

Venkatraman Gopalan (Pennsylvania State University), **Jingyang He** (Pennsylvania State University), **Rui Zu** (Pennsylvania State University), **Seng Huat Lee** (Pennsylvania State University), **Abhishek Kannan Iyer** (Northwestern University), **Victor Trinquet** (U C Louvain), **Guillaume Brunin** (U C Louvain), **Geoffroy Hautier** (Dartmouth University), **Gian-Marco Riganese** (U. C. Louvain), **Mercouri Kanatzidis** (Northwestern University), **Zhiqiang Mao** (Pennsylvania State University)

Keywords: Characterization, Growth, Modeling; Bulk; chalcogenides, pnictides; Flux Growth, Melt Growth, VPE; Nonlinear; Optical Materials, Quantum Materials

The ability to combine and split photons using nonlinear optical (NLO) interactions has had a dramatic impact on generating a continuously tunable electromagnetic spectrum from x-rays to ultraviolet, visible, infrared and THz. This has revolutionized both fundamental science as well as technological applications ranging from spectroscopy to medical imaging, optical communications, environmental monitoring, aviation and gravitational wave detection. We are presently at the threshold of a new era of quantum communications; here nonlinear optics remains the primary means to generate entangled photons, and the need for large single photon nonlinearity is urgent. However, a grand challenge remains: the workhorse nonlinear optical crystals currently are a handful; their dearth is even more severe in the infrared(>2Î¼m) and in the ultraviolet(<400nm). A key challenge is the many competing demands placed on an NLO crystal, e.g large nonlinearity with large bandgap (Eg) among many others. The PI however believes that the field is currently poised for a breakthrough: Several theory-guided predictions of new compositions using machine learning and density functional theory have begun appearing. Further, inorganic chemists have indeed discovered hundreds of promising NLO compounds over the years that have not transitioned past promising studies in their powder form to single crystals. Single crystal growth, full optical tensors characterization, and open-source NLO modeling software proposed are critical first steps to making this leap into a new generation of nonlinear optical sources and devices. This talk will present a few such recent discoveries of infrared second-order nonlinear optical crystals as well as a new nonlinear optical modeling called #SHAARP.

Ternary chalcopyrite semiconductors for mid-IR laser applications

Peter Schunemann (BAE Systems, Inc.), **Kevin Zawilski** (BAE Systems, Inc.)

Keywords: Growth; I-III-VI and II-IV-V; Melt Growth; Nonlinear; Optical Materials

The ternary chalcopyrite semiconductors $AgGaS_2$, $AgGaSe_2$, $ZnGeP_2$, $CdGeAs_2$, and most recently $CdSiP_2$ are among the most efficient and widely-used nonlinear optical (NLO) crystals for mid-infrared frequency conversion involving interaction wavelengths beyond 4 microns. Here we survey the entire class of chalcopyrites â€“ including II-IV-V2, I-III-VI2, and II-III2-VI4 (defect chalcopyrites) â€“ in search of promising new NLO crystals offering high nonlinear coefficients, broad transparency ranges, low absorption losses, adequate birefringence for phase matching, and ideally congruent melting to allow for growth from stoichiometric melts by directional solidification. We report preliminary results on compound synthesis of the most promising candidates by direct- or two-temperature vapor transport, and subsequent crystal growth using the horizontal gradient freeze technique in transparent furnaces. Phase identification and crystallographic orientation were determined by x-ray diffraction, and spectral transmission of polished samples was determined using a UV/VIS/NIR spectrophotometer (0.5-3 microns) and an FTIR spectrometer (2-25 microns),

Growth of BaGa4S7 and BaGa4Se7: new broad-band nonlinear crystals for the mid-infrared

Peter Schunemann (BAE Systems, Inc.), **Kevin Zawilski** (BAE Systems, Inc.)

Keywords: Growth; II-III-VI Chalcogenides; Melt Growth; Nonlinear; Optical Materials

Barium thiogallate (BaGa4S7, BGS) and barium sellenogallate (BaGa4Se7, BGSe) have emerged in recent years as attractive new nonlinear optical (NLO) crystals notable for the rare combination of a wide band gap (3.54 eV and 2.64 eV respectively), long phonon cut-off wavelengths (13.7 ï□m and 18 ï□m respectively), and relative ease of growth from stoichiometric melts. Their large band gaps favor high damage thresholds and allow for pumping with widely-available 1-micron laser sources without two-photon absorption, and their nonlinear coefficients (5 pm/V and 20 pm/V respectively) are comparable with the best oxide NLO crystals but with greatly extended IR transparency. The low symmetry of these crystals - BGS is orthorhombic (point group mm2) and BGSe is monoclinic (point group m) - makes orientation and fabrication of phase-matched devices more challenging compared to uniaxial crystals. To simplify this process, and to maximize the yield of oriented frequency conversion samples from single crystal boules, we oriented seed crystals with the tuning axis normal (vertical) to the top surface of the seed and resulting boule, and the growth axis along or near the phase-matching direction. Each compounds was synthesized from high-purity elemental starting materials by two-temperature vapor transport, followed by seeded horizontal gradient freeze (HGF) growth in transparent furnaces, yielding single crystals up to 30 mm in diameter by 150 mm in length. Phase-matched samples were cut, polished, and AR-coated with apertures up to 12 x 12 mm2 and lengths greater up to 18 mm.

Absorption and Defects Related to High Average Power Operation of $CdSiP_2$ Crystals

Kevin Zawilski (FAST Labs, BAE Systems), **Peter Schunemann** (BAE Systems), **Jani Jesenovec** (BAE Systems), **Lindsay Radl** (BAE Systems), **Spencer Horton** (BAE Systems), **Tim Gustafson** (Air Force Institute of Technology, Wright-Patterson AFB), **Larry Halliburton** (University of West Virginia), **Nancy Giles** (Air Force Institute of Technology, Wright-Patterson AFB), **Kent Averett** (Air Force Research Laboratory, AFRL/RX), **Jon Slagle** (Air Force Research Laboratory, AFRL/RX)

Keywords: Characterization, Defects, Growth; Bulk; chalcopyrite; Melt Growth; Nonlinear; Optical Materials

CdSiP2 (CSP) is a nonlinear optical chalcopyrite semiconductor developed as a wider-band-gap analog of ZnGeP2 (ZGP) to enable mid-infrared generation with widely-available 1- and 1.55-micron pump laser sources. CSP exhibits the highest d-coefficient (d_{36} = 85 pm/V) among all practical nonlinear optical crystals. ZGP is close with d_{36}=79 pm/V. CSP has a lower thermal conductivity than ZGP (13.6 W/mK vs 35 W/mK for ZGP) which is more than offset by nearly 10-fold lower absorption losses in the 1.06- to 2.1-micron wavelength range, making CSP an attractive alternative to ZGP even for 2-micron-pumped OPO power-scaling. Although CSP growth presents significant crystal growth challenges compared to ZGP, recent advances in crystal growth from stoichiometric melts using the horizontal gradient freeze (HGF) technique have resulted in improved yields of crack- and twin- free single crystals. CSP parts with apertures up to 10 x 10 mm^2 have been fabricated, as well as phase matched OPO parts with interaction lengths greater than 20 mm. Characterization of CSP crystals for high average power 2-micron pumping operation was performed using an OPO seeded OPA train with a pump laser operating at > 130W average power at 2.09 microns with 22 ns pulse widths and 10 KHz rep rate. ZGP and CSP crystals were substituted in the OPA train to directly compare the thermal lensing present in CSP versus ZGP phased matched parts. Electron paramagnetic resonance (EPR) analysis was used to identify potential point defects responsible for absorption in CSP crystals both near 2 microns and closer to the band edge at 1 micron. Multiple EPR samples from one CSP crystal were used to determine defect distribution along the length of a grown crystal. Strategies and initial results for eliminating or compensating for these defects via modifications to the growth process or post-growth annealing will be discussed.

Invited Talk

Anisotropic thermal properties of CdSiP2 crystals

Shekhar Guha (Air Force Research Laboratory), **Joel Murray** (Air Force Research Laboratory), **Michael Susner** (Air Force Research Laboratory), **Emmanual Rowe** (Air Force Research Laboratory), **Michael McLeod** (Air Force Research Laboratory), **Kevin Zawilski** (BAE Inc.), **Peter Schunemann** (BAE Inc.)

Keywords: Characterization; Bulk; phosphide compound; Nonlinear; Optical Materials

CdSiP2 is one of the primary candidate materials for frequency conversion application. An attractive feature of CdSiP2 is that it can be pumped with short wavelength lasers where higher laser power and energy are available. However, absorption and heating of the crystal is also higher at short wavelengths which limit efficient frequency conversion. Since thermal conductivity is a key parameter that determines crystal heating through light absorption, it is important to know the thermal conductivity values, especially as a function of temperature and crystal orientation. Although thermal conductivity of CdSiP2 has been measured before (1), a detailed study of the temperature and orientation dependence is not easily available in the literature. The thermal diffusivity (Î±) and specific heat capacity (cp) of CdSiP2, measured in a contactless way over a temperature range from 173 to 473 K by the flash analysis technique will be presented. The instrument used for the measurement is a NETZSCH Flash Analyzer LFA 467 HyperFlash E 1461. designed as a vertical system with a plane parallel sample placed in the center. An embedded Xenon lamp placed at the bottom is used as a flash source to generate a short (20 to 1200 Âµs) duration pulse which is absorbed at the bottom face of the sample. The temperature rise on the opposite side is monitored without contact with the sample as a function of time by a infrared HgCdTe detector placed at the top of the system. The detector allows measurements of the time of the heat transfer from one side to another at temperatures ranging from 173 to 773 K. Specific heat measurements are done by differential scanning calorimetry (DSC) using the Evercool 1 Physical Property Measurement System (Quantum Design, Inc., USA) with a heat capacity option. References: [1] Growth and characterization of large CdSiP2 single crystals, Kevin T. Zawilski, Peter G. Schunemann, Thomas C. Pollak, David E. Zelmon, Nils C. Fernelius and F. Kenneth Hopkins, Journal of Crystal Growth, Volume 312, Issue 8, 1 April 2010, Pages 1127-1132

Poster

Characterization of Growth Sectors in Gallium Nitride Substrate Wafers

Yafei Liu (Stony Brook University), **Shanshan Hu** (Stony Brook University), **Zeyu Chen** (Stony Brook University), **Qianyu Cheng** (Stony Brook University), **Balaji Raghothamachar** (Stony Brook University), **Michael Dudley** (Stony Brook University)

Keywords: Characterization, Defects, Growth; Bulk; III-Vs (Traditional), Nitrides; Solution Growth, VPE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Gallium Nitride (GaN) is one of the most promising wide band gap semiconductor materials that are replacing silicon (Si) in power electronic applications. However, the quality of the material is limiting its application in high performance power electronic materials. Several bulk crystal growth methods have been developed including physical vapor transport (PVT) method [1, 2], Na-flux method [3], ammonothermal method [4, 5], and hydride vapor phase epitaxy (HVPE) method [6]. Moreover, patterned HPVE growth methods template [7] have been developed to further lower the dislocation densities. Among these growth methods, Ammonothermal and patterned HVPE have shown promising crystal quality for power device applications [8-10]. The ammonothermal grown GaN shows overall high quality with a dislocation density as low as 103 cm-2. The patterned growth method can concentrate dislocations to small areas leaving the remaining regions relatively dislocation-free (< 102 cm-2). Recent synchrotron X-ray topography studies have revealed domain features in both ammonothermal and patterned HVPE GaN wafers. Using synchrotron X-Ray Plane-Wave Topography (SXPWT, previously known as synchrotron X-Ray Rocking Curve Topography), these domain features that have enclosed diamond or quadrilateral shapes have relative compressive strain values (~ 10-5). These features are visible on SEM micrographs using a Robinson detector (RBSD). The origin of these strains is likely different impurity incorporation rates in different growth sectors. In patterned HVPE grown method, it has been reported that growth sectors exist due to growth along different directions [11]. A similar situation is likely for the ammonothermal substrates as well although no studies on that have been reported. Information on the nature of these domain areas is important as these regions are supposed to be used in device fabrication. To characterize the difference in impurity concentrations in these domains, SIMS measurements are currently being carried out. These results will be discussed to confirm the origin of the strain. [1] H. Wu, J. Spinelli, P. Konkapaka, M. Spencer, MRS Online Proceedings Library Archive 892 (2005). [2] D. Siche, D. Gogova, S. Lehmann, T. Fizia, R. Fornari, M. Andrasch, A. Pipa, J. Ehlbeck, Journal of crystal growth 318 (2011) 406-410. [3] M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. DiSalvo, Journal of crystal growth 242 (2002) 70-76. [4] R. DwiliÅ „ski, R. DoradziÅ„ski, J. GarczyÅ„ski, L. Sierzputowski, A. Puchalski, Y. Kanbara, K. Yagi, H. Minakuchi, H. Hayashi, Journal of Crystal Growth 310 (2008) 3911-3916. [5] T. Hashimoto, F. Wu, J.S. Speck, S. Nakamura, Journal of Crystal Growth 310 (2008) 3907-3910. [6] H.P. Maruska, J. Tietjen, Applied Physics Letters 15 (1969) 327-329. [7] T. Nakamura, K. Motoki, GaN substrate technologies for optical devices, IEEE, vol 101, 2013, p. 2221. [8] B. Raghothamachar, Y. Liu, H. Peng, T. Ailihumaer, M. Dudley, F.S. Shahedipour-Sandvik, K.A. Jones, A. Armstrong, A.A. Allerman, J. Han, H. Fu, K. Fu, Y. Zhao, Journal of Crystal Growth 544 (2020) 125709. [9] Y. Liu, B. Raghothamachar, H. Peng, T. Ailihumaer, M. Dudley, R. Collazo, J. Tweedie, Z. Sitar, F.S. Shahedipour-Sandvik, K.A. Jones, Journal of Crystal Growth 551 (2020) 125903. [10] Y. Liu, H. Peng, T. Ailihumaer, B. Raghothamachar, M. Dudley, Journal of Electronic Materials 50 (2021) 2981-2989. [11] K. Motoki, T. Okahisa, S. Nakahata, N. Matsumoto, H. Kimura, H. Kasai, K. Takemoto, K. Uematsu, M. Ueno, Y. Kumagai, Journal of Crystal Growth 237 (2002) 912-921.

Poster

Investigation of non-destructive and non-contact electrical characterization of GaN thin film on ScAlMgO4 substrate using THz-TDSE with characteristic impedance analytical model

Hayato Watanabe (Ritsumeikan Univ.), **Dingding Wang** (Ritsumeikan Univ.), **Takashi Fujii** (Ritsumeikan Univ., PNP, Fukuda Crystal Lab.), **Momoko Deura** (R-GIRO), **Toshiyuki Iwamoto** (PNP), **Tsuguo Fukuda** (Fukuda Crystal Lab), **Tsutomu Araki** (Ritsumeikan Univ.)

Keywords: Characterization, Technology/Equipment; Thin Film; Nitrides; MBE; Energy Materials, Sustainable Materials

ScAlMgO4 (SAM) has attracted attention as a substrate for the growth of gallium nitride (GaN). Our group aims to fabricate GaN freestanding substrates by growing a 1 Âµm GaN thin film as a template on a SAM substrate by RF-MBE followed by HVPE growth of GaN on the template with a thickness in the order of mm. We have proposed Terahertz Time-Domain Spectroscopic Ellipsometry (THz-TDSE) as a non-destructive and non-contact characterization method for the RF-MBE-grown thin film template. THz-TDSE is a method to analyze the film thickness and electrical properties (resistivity, carrier density, and mobility) of a sample by fitting the ellipsometric parameters tanÎ¨ and Î”, which represent the change in polarization state due to reflection of THz waves, to an analytical model. We have shown that the electrical properties and film thickness can be determined simultaneously for GaN films about 3 Î¼m thick. For a GaN film of about 1 Î¼m thickness, the electrical property values were obtained when the film thickness was fixed. However, when the film thickness was added to the fitting parameters, there were multiple optimal solutions, and it was found to be difficult to uniquely determine the optimal solution. In this study, we investigated the application of a model using characteristic impedance (CI model) to accurately determine electrical properties and film thickness in a single step. The CI model requires only scattering time and sheet resistance as fitting parameters, and does not require film thickness, background dielectric constant, or effective mass, which are necessary in the FR model. Thus, it is considered that electrical properties and film thickness can be obtained at single time by obtaining electrical properties with the CI model and applying them to the FR model. Although the CI model has been shown to be valid for graphene, its applicability to thin films of 3D materials has not been determined. Therefore, we applied the CI model to THz-TDSE measurements of a 1 Âµm thick GaN film on a SAM substrate and examined its validity. The results of the analysis showed that the electrical properties obtained by the FR and CI models were in close agreement with the electrical measurements of the Hall effect measurement, and the film thickness was close to the value observed in the cross-sectional TEM.

Invited Talk

Engineered Substrates: Understanding structure and defects through x-ray and electron-based characterization techniques

Mark Goorsky (UCLA), **Michael Liao** (Naval Research Laboratory), **Kenny Huynh** (UCLA), **Kaicheng Pan** (UCLA), **Lezli Matto** (UCLA)

Keywords: Characterization; Thin Film; Nitrides, Novel, Oxides; UWBG/WBG Semiconductor; Energy Materials, Optical Materials, Quantum Materials

Heterogeneous integration provides new layered structures that rely on the transfer of bulk or epitaxial layers to an alternative substrate. The transfer process involves bonding, implant-induced exfoliation or grinding, and polishing to produce single or multiple layer stacks of single crystal layers with specific orientations. Although silicon-on-insulator structures have matured into widely used commercial products, other applications are in much earlier stages of research and development. Here, the transfer of wide bandgap semiconductors to alternate substrates and the formation of piezoelectric on insulator structures are examined for the presence of defects and the impact of these defects on device performance. The control and elimination of defects for the key processing steps will be assessed with a focus on using high resolution x-ray scattering and transmission electron microscopy measurements.

Invited Talk

Growth and characterization of pure and substituted rare-earth orthoferrite single crystals

Suja Elizabeth Saji (Indian Institute of Science), **Bhawna Mali** (Indian Institute of Science)

Keywords: Characterization, Growth; Bulk, Single Crystal; Orthoferrites, Oxides; Melt Growth, floatzone growth; Magnetic spin ordering; Spin reorientations

Rare-earth oxides such as manganites and orthoferrites continue to spark researchersâ€™ interest due to the formation of novel electric and magnetic phases and potential applications. Rare-earth compounds with very high melting points are best grown by the crucible-less float-zone technique. Cationic substitutions further enhance characteristic phases and fine-tune the desired properties. In powder and ceramic forms, the crystallites orient randomly in different directions and present an average effect of anisotropic properties, whereas single crystals enhance this effect in specific orientations. By ionic substitution, it compounds with additional impurity phases and structural deformations. By concomitantly applying a zone refining process to the floating zone growth, one can minimise or eliminate impurity phases to a great extent [1, 2]. The trace impurities separate due to differences in segregation coefficients and directional solidification of the pure material, which yields pure crystals that are reliable to use without fear of impurity influences. Besides details of growth, we will report the results of standard characteristic measurements of Laue spectroscopy, XRD, and EPMA, to assess the crystallinity, orientation, phase purity and composition of few R(1-x)Rxâ€™FeO3 bulk crystals. We determined the oxidation states of the substituted ions using x-ray photoelectron spectroscopy measurement to evaluate their role in physical characteristics. We will discuss, in detail, the unusual spin configurations that evolve consequentially in a few phase-pure rare earth orthoferrites. [1] Z. Zhang et. al. Crystal growth. PNAS Vol.96 No. 20 [2] Bhawna Mali et. al, Phys. Rev. B 105, 214417

Invited Talk

The comprehensive synchrotron topography and rocking curve imaging capabilities at the Advanced Photon Source

XianRong Huang (Argonne National Laboratory), **Michael Wojcik** (Argonne National Laboratory), **Lahsen Assoufid** (Argonne National Laboratory)

Keywords: Characterization; Bulk; Carbides, Nitrides, Oxides, Silicon; PVT; Energy Materials

The 1-BM beamline at the Advanced Photon Source (APS) is a bending magnet beamline with a large X-ray beam size of 80 mm by 3 mm. It has comprehensive synchrotron topography imaging capabilities for characterization of bulk and epitaxial crystals. The beamline is equipped with a white-beam topography stage with fully automated angular and scanning motors for fast imaging of up to 7-inch wafers. It has a double-crystal set-up, of which the second stage can be used for monochromatic-beam topography either in the stepped/continuous rotation mode (for recording the overall or integrated images of bent crystals) or in the single-exposure model. The first stage has different beam conditioners in the grazing-incidence geometry that can expand the vertical beam size from 3 mm to ~100 mm for double-crystal rocking curve imaging and diffraction. When the Bragg angles of the sample and the beam conditioner are identical or very close to each other, the measured rocking curve of the sample is almost the intrinsic Darwin width of the sample (for perfect crystals). Compared to other diffraction techniques, therefore, the rocking curve imaging technique provides the highest strain (or angular) sensitivity in the order of 10^{-6} (or micro-radian) that can reveal tiny strains (of defects) and lattice mismatch [1]. The beamline also provides a variety of supporting software or computer tools for data analyses, including the LauePt program [2] for indexing Laue patterns, the HXRD program for calculating Darwin curves and convoluted rocking curves, tools for analyses of rocking curve images, and the computer model/code for simulation dislocation contrast [3]. Extensive characterization work has been carried out at the beamline for wide-bandgap semiconductors SiC, GaN, AlN, Ga2O3, etc. In this talk, we will give an overall introduction to these capabilities and activities. We will also introduce our post-APS-Upgrade plans for further improvement and development of the beamline, including the novel multiple-beam diffraction method for accurate measurements of in-plane lattice mismatch of epitaxial crystals [4]. [1] S. Stoupin et al., AIP Conf. Proc. 1741, 050020 (2016). [2] X.R. Huang, J. Appl. Cryst. 43, 926 (2010). [3] H. Peng et al., J. Appl. Cryst. 55, 544 (2022). [4] X.-R. Huang et al., Appl. Phys. Lett. 105, 181903 (2014).

Step-bunching on 4H-SiC (000-1) in Si based solutions at 1873 K during interface reconstruction

Takeshi Yoshikawa (Osaka University), **Hideto Aoki** (Institute of Industrial Science, The University of Tokyo), **Didier Chaussende** (University of Grenoble Alpes, CNRS, Grenoble INP, SIMAP), **Sakiko Kawanishi** (Kyoto University), **Takeshi Mitani** (National Institute of Advanced Industrial Science and Technology)

Keywords: Fundamentals, Technology/Equipment; Bulk; Carbides; Solution Growth; Energy Materials

To control smooth interface avoiding step-bunching and the subsequent solvent inclusions is a great issue during the solution growth of high quality SiC crystals. It is well known that step-bunching greatly differed when using different solvents, and even small additive such as Al in solvents significantly influenced the step-bunching. To understand the step and solvent interaction at the growth interface, we study the interface reconstruction where a saturated solution is placed on the vicinal surface of 4H-SiC (000-1) substrate in the isothermal field and step-bunching occur without macroscopic growth and dissolution. In the present work, we performed the interface reconstruction experiment on Si and Si-40mol%Cr solvents to understand the kinetics of the initial step-bunching on the vicinal interface of 4H-SiC (000-1). Then, we also examined the interface reconstruction for the various binary solvents. The step bunching was progressed to form the meandered steps for the binary solvents alloyed with elements on the right side of the periodic table whereas the step bunching was suppressed for the solvents alloyed with elements on the left side of the table. In the presentation, detailed discussion on the tendency of step bunching will be given with the thermodynamic properties of the elements.

Effective Penetration Depth Analysis of Dislocations Lying on the Basal Plane in Grazing Incidence Synchrotron X-ray Topographs of 4H-SiC Wafers

Qianyu Cheng (Stony Brook University), **Shanshan Hu** (Stony Brook University), **Zeyu Chen** (Stony Brook University), **Yafei Liu** (Stony Brook University), **Balaji Raghothamachar** (Stony Brook University), **Michael Dudley** (Stony Brook University)

Keywords: Characterization, Defects; Bulk; Carbides; PVT; UWBG/WBG Semiconductor; Energy Materials

Synchrotron X-ray topography (XRT) is a powerful characterization technique that has been widely applied for semiconductor industry including bulk crystals, epitaxial films, and wafers for electronic device fabrication [1, 2]. It is a non-destructive approach which produces high-resolution images of the internal structure of a crystal through X-rays generated by a synchrotron radiation source. This provides valuable insights into the crystal defects and structural features that govern the properties and behavior of the material. For 4Â° off-axis (0001) 4H-SiC wafers, the grazing-incidence geometry topographic technique is commonly employed where the X-ray beam is directed onto the sample with a small incidence angle (~1-2Â°). This setup is particularly useful to study dislocations lying on the basal plane as information on defects from within the effective penetration depth of X-rays is exclusively revealed. Therefore, Therefore, it is essential to establish a proper procedure to define this effective penetration depth as that enables three-dimensional dislocation configuration analysis and accurate density calculation. This study aims at developing a universal method that determines the effective penetration depth of all types of dislocations lying in the basal plane with different Burgers vector and line direction. The dislocations studied include classic basal plane dislocations (BPDs) as well as Frank type dislocations created through deflection of threading screw/mixed dislocations (TSD/TMD) onto the basal plane. Those defects are considered as particularly deleterious which can cause degradation that challenges device reliability while achieving high performance [3, 4]. Investigation combines synchrotron monochromatic beam grazing-incidence XRT in (11-28) reflection with comprehensive ray-tracing simulation [5] incorporating the effect of surface relaxation [6] and X-ray absorption [7, 8]. Quantitative analysis was performed on BPDs and Frank type dislocations with different Burgers vector and line directions combination by comparing topographically observed dislocation features with simulation contrasts. Analysis of the results reveals that the observable dislocation contrast depends on the effective misorientation associated with the dislocation modulated by the photoelectric absorption effect. A simplified model based on an approximate expression for the effective misorientation associated with a dislocation modulated by the photoelectric absorption effect is proven effective to estimate the effective penetration depth for both BPDs and Frank type dislocations with c component of Burgers vector. This simplified model can be used as an alternative method to the full ray tracing simulation approach. Reference: 1. B. K. Tanner, D. K. Bowen, Synchrotron X-radiation topography, Mater. Sci. Rep. 8 (1992), 369-407 2. A R Lang, 26 (1993) J. Phys. D: Appl. Phys. A1-A8 3. H. Tsuchida, et al, Phys. Status Solidi B 246 (2009) 1553-1568. 4. P. G. Neudeck, Mater. Sci. Forum 338-342 (2000), 1161-1166. 5. X.R. Huang, et al, J. Appl. Cryst. 32 (1999) 516-524. 6. H. Peng, et al, J. Appl. Cryst. 54 (2021) 439-443. 7. F. Fujie, et al, Acta Mater. 208 (2021) 116746. 8. T. Ailihumaer, et al, Mater. Sci. Eng.: B 271 (2021) 115281.

Invited Talk

Measurement of temperature-dependent refractive indices and absorption coefficients of ZnSe and ZnTe

Shekhar Guha (Air Force Research Labortory), **Jean Wei** (Air Force Research Labortory), **Joel Murray** (Air Force Research Labortory), **Peter Stevenson** (Air Force Research Labortory)

Keywords: Characterization; Bulk; II-VI; Nonlinear; Optical Materials

Zinc selenide (ZnSe) and zinc telluride (ZnTe) are important chalcogenide optical materials which have many applications, especially in nonlinear optics and electro-optics. In many such applications it is important to know the temperature dependence of the optical properties, especially the refractive index (n) and the absorption coefficient (Î±) in the near band gap region. In a compilation of earlier work (1), refractive index values and Sellmeier fits for ZnSe were presented for the wavelength range of 0.55-18 Î¼m over a temperature range of 93-618 K, and for ZnTe at room temperature in the wavelength range of 0.55-30 Î¼m. In a more recent work [2], the n and Î± values of ZnSe films (thicknesses ranging from 50-800 nm) deposited on transparent quartz substrates are provided over the wavelength range of 0.3-2.5 Î¼m. However, the temperature-dependent n and Î± were not studied in this work [2]. To our knowledge, the temperature-dependent n and Î± values for ZnTe have not been presented earlier. Common optical characterization methods used for the determination of n and Î± include spectroscopic ellipsometry, interferometry, and transmission measurementsâ€"each of which have shortcomings when employed on their own. However, combination of all three measurement techniques for a given material can provide necessary optical property values over a broader spectral and temperature range vs. each measurement technique used individually. Here, we combine these three optical measurement techniques to determine the temperature-dependent n and Î± of commercially purchased ZnSe and ZnTe wafers in the wavelength range of 0.5-3 Î¼m over the temperature range of 80-450 K.. Temperature-dependent Sellmeier coefficients are obtained for both materials. 1. Refractive Index of ZnS, ZnSe, and ZnTe and Its Wavelength and Temperature Derivatives, H. H. Li, Journal of Physical and Chemical Reference Data, 13, 103 (1984) 2. Analysis of thickness influence on refractive index and absorption coefficient of zinc selenide thin films, G. Georgescu* and A. Petri, Optics Express, 27, 34803 (2019)

Invited Talk

In situ observation of growth behavior of small-angle grain boundaries in multicrystalline silicon during directional solidification

Lu-Chung Chuang (Institute for Materials Research, Tohoku University), **Kozo Fujiwara** (Institute for Materials Research, Tohoku University)

Keywords: Characterization, Defects, Growth; Bulk; Silicon; Melt Growth; Nonlinear

Grain boundaries (GBs) are two-dimensional defects, which are planes of mismatched atomic structure. They define multicrystalline materials. Among various types of GBs, small-angle GBs (SAGBs) possess a misorientation typically less than 15Â°, and are well known as dislocation arrays. SAGBs show interesting properties; however, their formation and growth behavior remain poorly understood. In this research, the growth behaviors of SAGBs in Si have been studied and directly observed in situ by an optical microscope during directional solidification. The GB characteristics and grain orientations have been identified by EBSD after solidification. Preferential etching was adopted to delineate the dislocation distribution on the surface of solidified samples. The combination of the above techniques enables investigations of SAGB growth behaviors and their interactions with dislocations. We have found: (1) SAGBs are capable of penetrating through Î£3 GBs at crystal/melt interface. Random GBs, which possess a misorientation of larger than 15Â°, do not exhibit similar behavior. This finding suggests that the dislocation structure in SAGBs plays a critical role in the GB penetration during solidification. (2) SAGBs are able to be generated by dislocation aggregation during growth. The alignment of dislocations reduces the elastic energy of individual dislocations and is thermodynamically more favorable to exist than randomly distributed single dislocations. (3) SAGBs act as dislocation sink during growth. It was found that dislocation clusters disappeared between two SAGBs, and the misorientation of both SAGBs increased simultaneously. This result implies that a SAGB is able to absorb dislocations during growth and alter its own interfacial structure with an increased misorientation. (4) Twist SAGBs have been observed splitting at crystal/melt interface and releasing tons of dislocations. These splitting occurred only at twist SAGBs with a boundary plane very close to {111}. SAGBs grew steadily without splitting with a boundary plane parallel to random orientations other than {111}. Since the {111} twist SAGBs are already known as crisscrossed dislocation networks, dislocation intersections in boundary plane are supposed to be heavily stressed. During directional solidification, the structural dislocations are possibly to climb to neighboring planes for preventing stress accumulation, and, as a result, a twist SAGB split due to dislocation climbing. Structural dislocations were released from boundary plane during this process, and more dislocations proliferated from GB splitting, as we have observed in the delineated sample surface. The facts found so far demonstrate that the growth behavior of SAGBs is related to dislocations significantly, and worth further study.

In-situ observation of 4H-SiC{0001} dissolution into molten alloy at 1500 K

Sakiko Kawanishi (Kyoto University), **Hiroyuki Shibata** (Tohoku University), **Takeshi Yoshikawa**

Keywords: Characterization, Fundamentals; Bulk; Carbides; Solution Growth; UWBG/WBG Semiconductor; Sustainable Materials

The melt-back process is an important pretreatment for seed crystals in growing high-quality SiC single crystals by solution growth. However, the phenomena surrounding the SiC dissolution into the solvent alloy during the melt-back process have not been clarified. In this study, the behavior of 4H-SiC{0001} dissolution into molten alloy was investigated by using high-temperature in-situ observation and the subsequent KOH etching. The effects of crystal polarity and doping conditions were studied through the visualization of the SiC/alloy interface at 1500 K. The bright-field and interference images were simultaneously captured using an optical microscope to clarify the in-plane morphology and step-height information, respectively. Local dissolutions with hexagonal pyramid-shape originating from threading screw dislocations (TSDs) were observed on the (000-1) face of n-type SiC with light nitrogen doping. The analysis of their behavior revealed that the process was governed by the spiral dissolution. In addition to the local dissolutions at TSDs, dissolutions originating from threading-edge dislocations were observed on the (0001) face of the same SiC crystal. Both polarity and doping conditions of the SiC crystals significantly affected to the shape of the local dissolution at the dislocations. Such local dissolutions may occur during the melt-back process and degrade the quality of grown crystals. Thus, the selection of the seed crystal is one of key issues to promote the melt-back while maintaining a smooth interface. In addition, it is important to maintain the interface undersaturation to be sufficiently small for obtaining the smooth interface during the melt-back.

Invited Talk

Development in Crystal Growth of PMN-PT Based Single Crystals

Jian Tian (CTS Corporation)

Keywords: Characterization, Growth; Bulk; Oxides; Melt Growth; Ferroelectric; Piezoelectric Materials

For the past 25+ years Bridgman growth technique has been used to grow lead magnesium niobate-lead titanate (PMN-PT) based single crystals, including binary PMN-PT single crystals and ternary PIN-PMN-PT (lead indium niobate-lead magnesium niobate-lead titanate) single crystals. Both crystals have been widely adopted in medical ultrasound imaging and selected underwater applications. With the increasing demand of single crystals and growing pressure on cost control, crystal manufacturers have put significant efforts in growing crystals with larger diameter, longer length, or more uniform crystal composition and property within a crystal to maximize part yield. Crystals of large diameter allows harvest of large parts and more parts from wafers. Availability of large parts promotes the adoption of single crystals where a large part is needed. Crystal usage increased sharply when large crystal parts can be produced from a single wafer. In addition, large parts help to improve transducer fabrication efficiency through batch processing. Crystal diameter increased from 25mm ~20 years ago to 100mm in production today. Efforts on 125mm diameter growth have been reported during the past several years. Progress on 125mm diameter crystal growth will be presented. Longer crystals can be achieved through different approaches. Earlier days as-grown crystals were short with a usable length of 20-25mm. Current production crystals have a usable length of ~50mm. The extra usable length of crystals is a result of longer crucible and more material charge to the crucible. There is a limit, however, on how long the usable portion of a crystal can grow with typical Bridgman growth. Crystal composition segregates during crystal growth. Actual usable length of a crystal is noticeably shorter than the total length of the crystal. As crucible gets longer, crucible is subject to greater hydrostatic pressure from the melt, which could lead to crucible failure. To further improve crystal usable length, a different approach, namely continuous feed crystal growth is needed. The initial charge of continuous feed crystal growth is less than a typical Bridgman growth. As a result, crucible does not experience high hydrostatic pressure or long hours of chemical attack from the corrosive melt. In addition, melt composition for the most part is kept constant by adding materials to the melt during crystal growth to balance change in melt composition from crystal growth. Continuous feed crystals with usable length up to 150mm have been grown. Growth result and crystal characterization will be presented.

Invited Talk

A Review of Single Crystal Underwater Transducers

Harold Robinson (Naval Undersea Warfare Center Division Newport)

Keywords: Devices; Bulk; Relaxor single crystals; Melt Growth; Piezoelecric; Piezoelectric materials

The unique material properties of lead magnesium niobate-lead titanate (PMN-PT) and lead magnesium niobate-lead indium niobate-lead titanate (PMN-PIN-PT) relaxor single crystals enable compact, broadband, high power sound projectors that cannot be realized using conventional ceramics. This paper shall highlight single crystal transducer prototypes developed at the Naval Undersea Warfare Center, Division Newport, and elsewhere demonstrating that the broadband, high power performance promised by single crystalâ€™s material properties can be realized in practical underwater transducers. Various single crystal transducer designs for underwater applications, including longitudinal vibrators, fully active and active-passive air-backed cylinder transducers, free-flooded ring transducers and bender bar transducers, will be presented. These transducer designs cover a wide span of frequencies, and utilize both 33- and 32-operating modes. Tuned bandwidths of up to 2.5 octaves of frequency, as well as source level increases of up to 15 dB at the band edges, will be demonstrated. It will also be shown that these technologies provide stable performance under high drive and duty cycle conditions. Finally, the impact of using these single crystal sources on the drive electronics and power consumption shall also be discussed.

Invited Talk

Motivation, Challenges and Potential Solutions in Characterisation of Bulk Piezoelectric Crystal Materials

Sandy Cochran (University of Glasgow), **Sakineh Fotouhi** (Nicola Fenu), **Abdul Hadi Chibli** (Yijia Hao), **Mingwei He** (Zhen Zhang), **Bo Liu** (Glasgow)

Keywords: Characterization, Modeling; Bulk; Oxides; Melt Growth; Ferroelectric; Energy Materials, Acoustic / ultrasonic materials

Finite element analysis (FEA) is favoured for 3D design of relaxor-PT single crystal devices and textured materials. However, successful implementation even under ambient conditions demands measurement of a complete elastopiezodielectric (EPD) matrix and this changes with temperature, pressure and applied electric field. Standard characterisation is based on electrical impedance spectroscopy (EIS) of multiple samples, each isolating one or two electroacoustic modes, with the results combined to obtain the EPD. However, this carries well-known disadvantages, with high costs contingent on the sample manufacture and accuracy contingent on variation between samples. Nevertheless, demand for new piezocrystals and increases in computing power for FEA are motivating work to obtain the EPD matrix in better ways. These include measurements on just one sample, often a cube of side several mm. However, this typically introduces the need for resonant ultrasound spectroscopy (RUS) to reduce the number of unknown properties, with EIS used for the others. Moreover, RUS procedures bring potential for further variation and the sample size may cause difficulty with preparation, poling and therefore measurement consistency. This paper discusses potential routes to miniature single-sample characterization (MSSC), with sample dimensions around 1 mm, bringing early promise for EPD matrix measurement with a single EIS measurement, enabling characterization under non-ambient conditions. As the characterization process is based on optimization, the approach relies on possibilities offered by new techniques utilizing artificial intelligence / machine learning (AI/ML). Piezoelectric materials have significant markets but the cost of development of the measurement techniques is prohibitive. However, algorithms already exist for problems with greater financial impact. One such algorithm, surrogate model-assisted differential evolution for antenna synthesis (SADEA), was developed for electromagnetic communications. With a conventional algorithm for characterization of [001]-poled PZ54 piezoceramic (CTS Ferroperm, Kvistgaard, Denmark) and lead-free PIC 700 (PI Ceramics, Lederhose, Germany) used as a reference, this approach is illustrated via a study of SADEA for the same materials, leading to consideration of piezocrystals. Our results suggest AI/ML-driven optimization may be applied efficiently for MSSC. Nevertheless, further work is required to determine the full range of materials to which it is applicable, including Mn-doped piezocrystals, and to extend it to the measurement of the EPD matrix in complex form to avoid approximation of losses with a conventional lumped model. Our ultimate target is to support virtual, rapid, accurate characterisation of piezocrystals using AI/ML-enabled software with single EIS measurements from single miniature samples.

Invited Talk

Process/Property Relationships of Textured Piezoelectric Ceramics for Acoustic Applications

Richard Meyer (The Pennsylvania State University), **Mark Fanton** (The Pennsylvania State University), **Josh Fox** (The Pennsylvania State University), **Brian Weiland** (The Pennsylvania State University), **Edward Oslosky** (The Pennsylvania State University), **Rick Gable** (The Pennsylvania State University), **Scott Brumbaugh** (The Pennsylvania State University), **Beecher Watson** (The Pennsylvania State University), **Christopher Eadie** (The Pennsylvania State University), **Chloe Fellabaum** (The Pennsylvania State University)

Keywords: Devices; Bulk; Oxides; Templated Grain Growth; Ferroelectric; Piezoelectric Materials

Directional tailoring of performance for oxide materials has been largely limited to taking advantage of anisotropies in single crystal materials. Polycrystalline materials with textured microstructures provides analogous performance improvements. Demonstration of property enhancement through textured microstructures has been demonstrated in ferroelectrics. This presentation summarizes the connections between processing, preferred alignment of the microstructure, and the electro-mechanical properties of the resulting material. The focus is primarily in the Mn-doped PMN-PZT family of materials. The engineering challenges associated with each step of the manufacturing process to yield tailored properties will be outlined and linked to the ability to control the process in a repeatable fashion. The electro-mechanical performance in terms of fundamental matrix parameters will be discussed in relationship to performance trade-offs of materials for both transmit and receive applications.

Invited Talk

Templated Grain Growth of High Performance Textured Piezoelectric Ceramics

Yongke Yan (Xi'an Jiaotong University), **Zhuo Xu** (Xi'an Jiaotong University), **Shashank Priya** (The Pennsylvania State University)

Keywords: Growth; Bulk; Oxides; Sintering; Ferroelectric; Energy Materials

High performance piezoelectric materials have attracted great attention from both the high-tech application and fundamental research due to wide applications as actuators, sensors, and transducers. Particularly, textured piezoelectric ceramics prepared by templated grain growth (TGG) process are highly demanded, considering of excellent performance similar to that of single crystal and low cost similar to that of random ceramics. During the TGG, the matrix particles nucleate and epitaxially grow on the aligned template microcrystals to control the grain orientation analogous to single crystals. In this talk, we first briefly describe the method of preparing textured piezoelectric ceramics, and then present several high-performance textured ceramics, including soft and hard relaxor-PT/PZT, $BiScO_3$-$PbTiO_3$, and bismuth layered structured high-temperature piezoelectric ceramics. At last, we highlight several representative characteristics of textured piezoelectric ceramics, such as high energy density dÂ·g, high piezoelectric voltage coefficient, near-ideal electromechanical coupling. These high-performance textured piezoelectric ceramics will have tremendous impact on design of ultra-wide bandwidth, high efficiency, high power density, and high stability piezoelectric devices, and will greatly promote the improvement of the performance of the next generation of piezoelectric devices.

Invited Talk

Textured $BiScO_3$-$PbTiO_3$ Piezoelectric Ceramics with both High Electromechanical Coupling Factor and High Curie Temperature

Fei Li (Electronic Materials Research Laboratory (Key Lab of Education Ministry), State Key Laboratory for Mechanical Behavior of Materials and School of Electronic Science and Engineering, Xiâ€™an Jiaotong University, Xiâ€™an, China.), **Mingwen Wang** (Xi'an Jiaotong University), **Shuai Yang** (Xi'an Jiaotong University), **Jie Wu** (Xi'an Jiaotong University), **Jinglei Li** (Xi'an Jiaotong University), **Liao Qiao** (Jiaotong University), **Xuechen Liu** (Jiaotong University), **Chao Wang** (Jiaotong University), **Xinya Feng** (Jiaotong University), **Chunchun Li** (Jiaotong University)

Keywords: Growth; Oxides; Sintering; Energy Materials

High-temperature piezoelectric devices require piezoelectric ceramics with high Curie temperatures to avoid the depolarization of piezoelectric ceramics during application. However, piezoelectric materials with high Curie temperatures usually have low piezoelectric properties, which limits the development of high-temperature piezoelectric devices. In the present work, to design piezoelectric ceramics with both high piezoelectricity and high Curie temperature, we used template-induced grain growth technology to fabricate $0.43BiScO_3$-$0.57PbTiO_3$ (BS-PT) ceramics with grains aligning along <001>c direction. The textured BS-PT ceramic was found to possess a high electromechanical coupling factor k_{33} of 81.2% and a relatively high Curie temperature of 402 oC. The electromechanical coupling factor k_{33} was much larger than that of conventional nontextured BS-PT ceramics (<70%). This work addresses a long-standing issue presented in BS-PT ceramics, i.e., the low electromechanical coupling property of BS-PT ceramics (k_{33}<0.70). The newly designed textured BS-PT ceramics are thought to be promising candidates for the design of high-temperature piezoelectric transducers and actuators.

Invited Talk

Synthesis and Characterization of High-TC Piezo-/Ferroelectric Single Crystals Based on Bismuth Scandate

Zuo-Guang Ye (Simon Fraser University), **Tara Nazari** (Simon Fraser University)

Keywords: Characterization, Growth; Bulk; Oxides; Flux Growth; Ferroelectric; Energy Materials

Today, there is an ever-growing demand for piezo-/ferroelectric materials that can operate at high temperatures for advanced technological applications. Current leading high-performance piezo-/ferroelectric materials like Pb(Mg1/3Nb2/3)O3 [PMN] suffer from low Curie temperature (TC), prohibiting them from properly functioning at high temperatures. Studies of the BiScO3-PbTiO3 [BSc-PT] system showed interesting ferroelectric features with a high TC and high coercive field (Ec). However, the piezoelectric coefficient needs to be further enhanced. An effective method for improving piezo-/ferroelectric properties is to incorporate a third component into the BSc-PT solid-solution. Our research group recently found that incorporating complex perovskite Bi(Zn1/2Ti1/2)O3 [BZT] into BSc-PT results in ceramics with excellent piezo-/ferroelectricity. However, no crystals have been available, which are expected to show even more desirable properties. In this work, we have grown the single crystals of BZT-BSc-PT by the high temperature solution method using PbO-Bi2O3-B2O3 as flux. The domain structure and phase transition in the grown crystals were investigated by polarized light microscopy (PLM). The Curie temperature was found to be 535 Â°C, making them promising materials for high temperature electromechanical transducer applications.

Invited Talk

Alternating current poled relaxor-PbTiO3 single crystals for ultrasound transducers

Xiaoning Jiang (NC State University), **Haotian Wan** (NC State University), **Huaiyu Wu** (NC State University), **Hwang-Pill Kim** (NC State University)

Keywords: (4th) Symposium on Ferroelectric Crystals and Textured Ceramics

Ferroelectric relaxor-PbTiO3 (PT) piezoelectric single crystals have been widely employed in a broad range of applications including ultrasound transducers due to their exceptionally high piezoelectricity and electromechanical coupling compared to its polycrystalline ceramic counterparts, i.e. Pb(Zr,Ti)O3 (PZT). Alternating current poling (ACP) as a domain engineering method has attracted much attention due to its further enhanced piezoelectric and dielectric properties in comparison to direct current poling (DCP) of relaxor-PT single crystals. Although ACP effectiveness has been successfully demonstrated for relaxor-PT single crystals with a variety of compositions, dimensions, and vibrational modes, ACP relaxor-PT single crystal devices have not been extensively investigated due to a lack of understanding on correlations between material properties and device performances. In this paper, ACP relaxor-PT single crystal ultrasound transducers are designed, fabricated and characterized. Comparative experiments regarding different vibration modes are also introduced to study what plays a critical role in the performances of ultrasound transducers. The initial ACP single crystal transducer prototype showed improved sensitivity (26%) and bandwidth at -6 dB (4%) over the DCP single crystal one. Therefore, devices with ACP single crystals are expected to have better resolution and dynamic ranges for imaging applications with improved performances.

Invited Talk

AC Poling Treatment over Tc in Grain-oriented BT-BNT Piezoceramics

Satoshi Wada (University of Yamanashi), **Zhuangkai Wang** (University of Yamanashi), **Sota Saito** (University of Yamanashi), **Ichiro Fujii** (University of Yamanashi), **Shintaro Ueno** (University of Yamanashi), **Kosuke Kawachi** (University of Yamanashi), **Minsu Kim** (University of Yamanashi), **Ryo Ito** (University of Yamanashi), **Hyunwook Nam** (University of Yamanashi)

Keywords: Fundamentals; Bulk; Oxides; Sintering; Ferroelectric

The engineered domain technique is one of the well-known domain engineering techniques for piezoelectric enhancement, which is composed of two parts, (1) domain wall fixing technique on the basis of crystallographic anisotropy and (2) increasing domain wall density on the basis of grain size control. This is because domain wall itself is very soft and possess very high dielectric and piezoelectric properties. For tetragonal perovskite oxide materials, crystallographic directions are <111> and <110> directions to fix domain walls into the materials. We previously reported the preparation of the <111> oriented barium titanate (BaTiO3, BT) ceramics using by electrophoresis deposition (EPD) method under high magnetic field (HM-EPD) of 12 T, and piezoelectric enhancement with d33 of 500pm/V. On the other hand, we also reported the preparation of the <110> oriented BT ceramics using by template grain growth (TGG) method, and piezoelectric enhancement with d33 of 800pm/V. However, the Curie temperature (TC) of BT is 132 ËšC, and this is very low for the most of piezoelectric applications, which need the higher TC over 200ËšC. Thus, in this study, we focus bismuth sodium titanate ((Bi0.5Na0.5)TiO3, BNT) â€“ BT (BNT-BT) system ceramics with high TC of around 250ËšC. Using tetragonal 0.85BNT-0.15BT chemical compositions, two kind of grain-oriented ceramics along <111> and <110> directions were prepared by different methods as reported for BT grain-oriented ceramics. These details will be presented at conference.

Invited Talk

Ferroelectric $BiFeO_3$-based epitaxial thin films with engineered domain structures for photovoltaic applications

Hiroki Matsuo (Kumamoto University), **Yuji Noguchi** (Kumamoto University)

Keywords: Characterization, Defects, Growth; Thin Film; Oxides; PLD; Ferroelectric; Energy Materials, Optical Materials

Ferroelectric materials that crystalize in polar point groups with switchable spontaneous electric polarization show a unique photovoltaic (PV) response that does not appear in the pn junction and Schottky junction. Quite high photovoltages, light-polarization-dependent photocurrents, and ultrafast photoresponse are attractive features for novel optoelectronic applications. The bulk PV effect that arises from spatial inversion symmetry breaking of polar crystal structures has been recognized as the origin of the PV response of ferroelectric materials. More recently, researchers found that multidomain ferroelectric crystals with high-density domain walls (DWs) show superior PV performance to single-domain crystals, and efficient photocarrier generation in DW regions by the DW-PV effect has been proposed. While previous studies suggested that domain engineering is a key technology to enhance the PV response of ferroelectric materials, however, roles of the DWs in the ferroelectric PV response are still unclear because of the lack of experimental investigations. In this study, we prepared ferroelectric Mn-doped $BiFeO_3$ (BFO) epitaxial thin films with single-domain and multidomain structures by the pulsed laser deposition (PLD) method to reveal the roles of DWs in ferroelectric PV response. Single-crystal substrates of $SrTiO_3$ with a miscut angle of 4 degrees and $DyScO_3$ are used for the deposition of the single-domain and multidomain samples, respectively. For the films grown on the $DyScO_3$ substrates, piezoresponse force microscope measurements and X-ray reciprocal space mapping revealed that films with a thin BFO buffer layer had an ordered multidomain pattern with periodic 71 deg. DWs whereas those without the buffer layer had randomly oriented domains. The Mn-doped BFO thin films with periodic DWs exhibited higher open-circuit voltages and photocurrent densities than single-domain films under visible light. Analyses of light-polarization angle dependence of the photocurrent density revealed that the DW-PV effect is the dominant origin of the enhanced PV response in the multidomain sample. This result indicates that Mn atoms in the DW regions act as an active center for exciton generation enhancing the visible-light response of DWs.

Invited Talk

Growth and characterization of PMN-PT crystals by vertical gradient freeze (VGF) technology

Guojian Wang (Luxium Solutions), **John Frank** (Luxium Solutions), **Peter Menge** (Luxium Solutions), **Danna Boughner** (Luxium Solutions)

Keywords: Ferroelectric

Relaxor ferroelectric Lead Magnesium Niobate-Lead Titanate (PMN-PT) crystal has been used in various applications such as medical ultrasound imaging, SONAR, micro-actuation and energy harvesting due to its high electromechanical coupling coefficient and high piezoelectric coefficient. However, the high cost of PMN-PT stems from low crystal growth yield and limits the wider its application. Vertical gradient freeze (VGF) is a crystal method requiring relatively simple equipment and producing high quality crystals with low dislocation densities and less impurity striations and facets. This method has been extensively used to grow semiconductor and optical crystals. Here, we reported the growth of Ï• 6â€□ PMN-PT crystals. The crystal structure, dielectric and piezoelectric properties of grown crystals were studied. The segregation of PT in VGF grown crystals is close to that in traditional Bridgman grown crystals. A method will be discussed to reduce the segregation of PT and increase the yield. This project is supported by Office of Naval Research (ONR) Contract N00014-18-C-1031 and N00014-21-C-1037, and Luxium Solutions.

Invited Talk

Crystal Growth of [100] Lead Zirconate Titanate (PZT) Crystals with composition Near the Morphotropic Phase Boundary by High Temperature Solution Growth

Vincent Fratello (Quest Integrated, LLC), **Son Won Ko** (Quest Integrated, LLC), **Wanlin Zhu** (The Pennsylvania State University), **Veronika Kovacova** (The Pennsylvania State University), **Susan Trolier-McKinstry** (The Pennsylvania State University)

Keywords: Growth; Bulk; Oxides; Flux Growth, Solution Growth; Ferroelectric, Piezoelectric; Ultraound

Lead zirconate titanate (PZT) is the dominant piezoelectric material in non-destructive testing applications because of its high efficiency and high-power capability but it is currently only available commercially as a ceramic. A single crystal has advantages in directionality and coherency over a randomly oriented or even a textured ceramic. Recent data on small flux-grown PZT crystals near the morphotropic phase boundary from Xie (Y. Xie, â€œSynthesis and Characterization of Piezo-ferroelectric Lead Zirconate-Titanate (PZT) Single Crystals and Related Ternary Ceramics,â€ Ph.D. thesis, Simon Fraser University, 2013) are an existence proof of the superior performance of single crystals as is seen in other piezoelectric material systems. PZT is non-congruent, meaning it cannot be grown from a melt of the same composition. Attempts to grow this material by flux/solution growth have been made over sixty years, but to date no scalable method of growing large single crystals of uniform composition has been developed, owing in part to the constraints of three-dimensional growth from a point nucleus, the difference in solubility between TiO_2 and ZrO_2, and unstable growth conditions from high flux evaporation. The composition of the grown crystals must be precise and uniform at or near the morphotropic phase boundary composition for good performance. A new method and melt composition for high temperature solution growth of undoped PZT single crystals has been developed and will be discussed in detail. The method enables growth of uniform and controllable compositions in a thermodynamically stable condition. Utilizing d spacing versus powder diffraction data, samples from early growth runs showed a near uniform composition $Pb(Zr_{0.522}Ti_{0.478})O_3$ with a uniformity of ï,±0.02 and the uniformity of the technique has been improved since. A variety of fluxes were tested and optimized and crystals up to 32 g in weight have been grown. While issues of flux vaporization, crystal uniformity and a stable crystal growth process have been solved, flux inclusions remain a challenge that influence crystal properties and performance.

Invited Talk

Enhanced piezoelectric properties and superior unipolar fatigue resistance in textured Pb(Mg1/3Nb2/3)O3-PbZrO3-PbTiO3 textured ceramics

Yunfei Chang (Harbin Institute of Technology), **Linjing Liu** (Harbin Institute of Technology), **Rui Lv** (Harbin Institute of Technology), **Qiangwei Kou** (Harbin Institute of Technology), **Hang Xie** (Harbin Institute of Technology)

Keywords: Growth; Bulk; Oxides; Sintering; Ferroelectric; Energy Materials

Piezoelectric ceramics with high and fatigue-resisted piezoelectric properties are required for various electromechanical applications. In this work, we fabricated highly [001]c-textured Pb(Mg1/3Nb2/3)O3-Pb (Zr, Ti)O3 ceramics through templated grain growth process. The effects of texture engineering on unipolar fatigue behaviors of the ceramics were investigated in terms of dielectric, ferroelectric, and piezoelectric properties. The textured ceramics with Lotgering factor F001 ~98% exhibited about 230% enhanced piezoelectric coefficient d33â˜— initially and substantially improved fatigue resistance during the entire unipolar cycling. Unipolar polarization Pmax and d33â˜— were nearly maintained up to 1000000 unipolar cycles in the textured ceramics, while 19% and 14% degradations were respectively observed from non-textured counterparts. Besides, much lower bipolar strain asymmetry Î³s~4% was observed from the textured samples fatigued after 1000000 unipolar cycles. The inherent fatigue anisotropy, weakened local bias fields and increased intrinsic contribution could all contribute to the substantially enhanced unipolar fatigue resistance. The enhanced piezoelectric properties and superior unipolar fatigue resistance make those textured ceramics promising for high-performance and robust piezoelectric actuator applications.

Invited Talk

Lead zirconate titanate ceramics with aligned crystallite grains

Jinglei Li (Xi'an Jiaotong University), **Fei** (Xi'an jiaotong university), **Shujun** (University of Wollongong)

Keywords: Fundamentals, Growth; Bulk; Oxides; Sintering; Ferroelectric; Energy Materials

The piezoelectric properties of $Pb(Zr,Ti)O_3$ (PZT) ceramics could be enhanced by fabricating textured ceramics that would align the crystal grains along specific orientations. We present a â€œseed-passivated texturing processâ€□ to fabricate textured PZT ceramics by using newly developed $Ba(Zr,Ti)O_3$ microplatelet templates. This process not only ensures the template-induced grain growth in Ti-rich PZT layers but also facilitates desired composition through interlayer diffusion of Zr/Ti. We successfully prepared textured PZT ceramics with outstanding properties, including Curie temperature of 360 Celsius, piezoelectric coefficients d_{33} of 760 picoCoulomb per Newton, g_{33} of 100 millivolts meter per Newton, and electromechanical coupling k_{33} of 0.85. The current study addresses the challenge of fabricating textured rhombohedral PZT ceramics by suppressing the otherwise severe chemical reaction between PZT powder and titanate templates.

Invited Talk

Development of Doped Relaxor-PT Ferroelectric Crystals at TRS

Jun Luo (TRS Technologies Inc (a subsidiaries of TAYCA Corporation)), **J**. **Moretz** (TRS Technologies Inc (a subsidiaries of TAYCA Corporation)), **K**. **Kitahata** (TRS Technologies Inc (a subsidiaries of TAYCA Corporation)), **Y**. **Sakano** (TAYCA CORPORATION), **S**. **Dynan** (TRS Technologies Inc (a subsidiaries of TAYCA Corporation))

Keywords:

The recent development effort at TRS was focused on two distinctively different ultrasound transducer applications. The first is the underwater sonar transducer applications. Based on the developmental demand for Navy sonar systems, the ferroelectric crystals are desirable if they can be operated under high electric field and high duty cycle. TRS has successfully grown <110>-oriented 75mm diameter Mn:PIN-PMN-PT single crystals, which are nearly free of voids. It is known that voids formation posted one of the biggest challenges in growth of high-quality Mn:PIN-PMN-PT single crystals. Through this effort, TRS not only overcame this issue, but also scaled up the crystal diameter from 50mm to 75mm, so largely increased the technology readiness for high powder and duty-cycle sonar transducers application.
The second frontier of development is the new generation relaxor-PT crystals for medical ultrasound imaging transducer application. It is known that TRS invented rare-earth (Re) doped relaxor-PT single crystal in collaboration with Penn State in 2018, which possess extremely high dielectric and piezoelectric performance(patent No.: US 11486055). In this work, one composition of Sm:PIN-PMN-PT has been down selected for medical ultrasound imaging transducer applications through an optimization process. The <001>-oriented 75mm diameter crystals have been successfully grown and characterized from this composition for the first time. Comparing to the undoped PIN-PMN-PT (TRS-X4B), dielectric permittivity of this type of Sm:PIN-PMN-PT crystals not only significantly increases at the beginning of the rhombohedral section, but varies much less through the whole rhombohedral section. The crystal also maintains the comparable coercive field to that of the undoped.

Poster

Growth and characterization of co-crystal of vanillin and hexamethylenetetramine for NLO application

Pooja Devi (National Institute of Technology Silchar), **Kintali Manohor Prasad** (National Institute of Technology Silchar), **Arindam Roy** (National Institute of Technology Silchar), **P. Srinivasan** (National Institute of Technology Silchar), **Suganya Devi K** (National Institute of Technology Silchar)

Keywords: Characterization, Growth; Bulk; Organic; Solution Growth; Nonlinear; Optical Materials

The non-linear properties of certain compounds play a vital role in the optical industries. The elements having a non-centrosymmetry space group with non-linear optical properties are the best for making single crystals. Some organic compounds exhibit large NLO responses, in many cases, orders of magnitude larger than widely known inorganic material. Vanillin with the chemical formula C8H8O3 possesses a phenolic aldehyde organic compound. Alternatively, vanillin is also known as 3-methoxy-4-hydroxy-benzaldehyde. Single crystal XRD analysis has confirmed that the grown crystal belongs to the monoclinic system with space group P21. Vanillin is an excellent material with higher second harmonic generation efficiency. So vanillin could be a good approach to make highly efficient single crystals. Hexamethylenetetramine with chemical formula C6H12N4 belongs to the cubic system with non-centrosymmetric space group I43m. From the literature survey, the co-crystal of vanillin and hexamethylenetetramine possess non-centrosymmetric orthorhombic space group Pca21. Colorless crystals were obtained via slow evaporation. The mixed solution of isopropanol and chloroform is used to obtain the required growth of the crystal. Similar crystals were also obtained using acetone, isopropanol, and propanol as solvents. Further, the formation of material will be confirmed quantitatively by FTIR, Hydrogen, and Carbon NMR spectral analysis. For the perfect percentage of transmission, UV-vis-NIR analysis will be done. The optical band gap, dielectric constant, and frequency can be further analyzed using these techniques. Kurtz Powder techniques will be used for the confirmation of second harmonic generation. Hence the co-crystal of vanillin and hexamethyleneteramine is a promising candidate for second-order non-linear applications.

Poster

Growth and characterization of metal derivative of 1,4-Diazobicyclo [2.2.2] octane (DABCO) for non-linear optical applications.

Arindam Roy (National Institute of Technology Silchar), **Kintali Manohar Prasad** (National Institutre of Technology Silchar), **P**. **Srinivasan** (National Institute of Technology Silchar), **Suganya Devi K**. (National Institute of Technology Silchar), **Saikatendu Deb Roy** (National Institute of Technology Silchar)

Keywords: Growth; Bulk; III-Vs (Traditional); Solution Growth; Nonlinear; Optical Materials

Examining and creating novel non-centrosymmetric metal-aided single crystals that have a strong potential for demonstrating nonlinear optical (NLO) applications. We report the synthesis of 1,4-diazobicyclo [2.2.2] octane (DABCO), a single crystal aided by Nickle (Ni). Using a conventional slow evaporation method, this material was produced at room temperature using methanol and water as solvents. Single crystal X-ray diffraction (SCXRD) will be used to confirm the single crystal NLO material structurally. Energy Dispersive X-ray Analysis (EDAX) verified the chemical makeup and existence of a Ni-aided single crystal. The newly synthesized crystal will be analyzed by UV-Visible study. Fourier transform infrared (FTIR) spectroscopy can identify the vibrations in the synthesized single crystal. The Vickers microhardness test can be used to determine the mechanical stability of the crystal. The material's electrical properties will also be subject to a dielectric investigation. The thermogravimetric/differential thermal analysis (TG/DTA) will be used to calculate and analyze the thermal stability. The crystal will undergo chemical etching in order to determine the etch pit. The Kurtz-Perry technique will be used to measure, analyze, and compare the second-order nonlinear susceptibility to KDP single crystal. The Z-scan method will be used to compute and analyze the third-order non-linear susceptibility.

Poster

Investigation on structural, elemental, spectral, thermal, mechanical, linear, and nonlinear optical nature of Rubidium hydrogen succinate dihydrate metal-organic single crystals

Kavitha S (VELLORE INSTITUTE OF TECHNOLOGY), **Ezhil Vizhi** (VELLORE INSTITUTE OF TECHNOLOGY)

Keywords: Growth; Solution Growth; Nonlinear

A metal-organic single crystal of Rubidium hydrogen succinate dihydrate (RbHSH) was grown using deionized water as a solvent by solution growth technique. The grown crystals were analyzed by elemental analysis, Single crystal X-ray diffraction was used to explore the structural characteristics of the developed RbHSH crystal. The crystalline nature of the title material was analyzed by powder X-ray diffraction analysis. Spectral studies have been carried out to investigate the modes of vibration in various chemical groups identified in RbHSH. A UV-visible transmittance study was carried out to determine the optical transparency of grown crystals, and it was discovered that the crystal was transparent across the visible-NIR range. The bandgap of the grown material is calculated by using Taucâ€™s relation. TGA-DSC were used to assess the thermal stability of the RbHSH compound. The work-hardening coefficient for various planes was calculated using the Vickers microhardness test, which reveals certain mechanical parameters like elastic stiffness constant (C11) and yield strength (Ïƒy) of the grown material. Etching studies were used to analyse the surface, and the etch pit density was estimated. The Z-scan approach were used to investigate the third order nonlinear optical (NLO) behavior of an RbHSH crystal. Keywords: Solution growth technique, XRD, etching study, linear and nonlinear property

Invited Talk

Growth of highly oriented, high-entropy transition metal disulfide (VNbMoTaW) Sx thin films

Cristian Ciobanu (Colorado School of Mines), **Koichi Tanaka** (UCLA), **Hicham Zaid** (UCLA), **Toshihiro Aoki** (UCI), **Aditya Deshpande** (UCLA), **Koki Hojo** (Nagoya University), **Christian Ratsch** (UCLA), **Suneel Kodambaka** (Virginia Tech)

Keywords: Fundamentals

As high-entropy alloying provides an increasingly important avenue for widening the set of functional materials for a variety of applications, it is useful to uncover synthesis routes that do not rely on large temperatures for their synthesis or for achieving entropic stabilization. We present the synthesis of novel, semiconducting, (VNbMoTaW)Sx ultra-thin films using ultra-high vacuum (UHV) sputter-deposition in Ar/H2S and Kr/H2S mixed gas atmosphere with 1 ~ 4% of H2S. We also show direct computational evidence from density functional theory calculations that high-entropy disulfide (HES) alloys with five cations from groups 4â€“6 are thermodynamically stable at temperatures routinely achievable in conventional deposition systems. While all 126 sulfide combinations with five group 4â€“6 transition metals are thermodynamically favorable at low (<800â€‰K) or medium (<1200â€‰K) temperatures, we show that electronegativities, valence electron concentrations, and atomic radii of cations can help predict whether an HES alloy is stable in the 1-H or the 1-T structure. These results demonstrate that a wide range of stable HES alloys can be synthesized experimentally as 2D layers, thereby providing facile ways for expanding the materialsâ€™ space with potential applications in electrochemical devices, catalysis, energy storage, or sensing.

Polymer Assisted Growth of Metal Nanoparticles for Sensing Applications

Chao Hsuan (Joseph) Sung (University of California, Irvine), **David Kisailus** (University of California, Irvine)

Keywords: Growth; nanomaterials; metals; electrospinning; sensing material

Toxic gases are commonly used in different types of industries and thus, present a potential health hazard. Therefore, highly sensitive gas sensing materials are essential for the safety of those operating in their environments. Though researchers have been working in this field for the past few decades to develop sensing materials with higher sensitivity, selectivity, and response times, there are still limitations. Currently, researchers have been developing gas sensors that utilize semiconducting metal oxides nanomaterials as the sensing elements. Many of these materials are synthesized in gas or solution phase and then integrated into sensing devices that operate based on changes in resistance upon gas absorption. However, these devices often have drawbacks due to discontinuities between nanoparticles. We have developed a sensing platform that consists of metal/metal oxide nanoparticles embedded within a continuous carbon / graphitic nanofiber network. However, the growth mechanisms of these nanoparticle-based structures, which nucleate within solid carbon scaffolds, have not been studied or documented extensively. In this study, we electrospin polymer solutions impregnated with transition metal ions to yield nanofibers that are annealed to form graphitic carbon / nickel nanoparticles based fibers for gas sensing applications. Metal based graphitic nanofibers are characterized through a combination of x-ray diffraction, transmission electron microscopy, as well as thermogravimetric analysis to reveal nucleation and growth processes that occur within the solid state. Multiple growth mechanisms are revealed and gas sensing experiments were conducted to demonstrate both synthesis-structure and structure-function relationships.

Invited Talk

Growth of metastable (Si)GeSn semiconductors

Oussama Moutanabbir (Department of Engineering Physics, Ecole Polytechnique de Montreal, Montreal, Quebec, Canada)

Keywords: Fundamentals; Low Dimensional

(Si)GeSn semiconductors are finally coming of age after a long gestation period. The demonstration of device-quality epi-layers and quantum-engineered heterostructures has meant that tunable all-group IV Si-integrated infrared photonics is now a real possibility. Indeed, this emerging family of semiconductors provides strain and composition as two degrees of freedom to independently engineer the lattice parameter and the band structure, in a similar fashion to the mature compound semiconductors. The prospect of mimicking IIIâ€“V and IIâ€“VI heterostructures and devices using all-group IV semiconductors on a Si platform has generated a great deal of interest motivated by the potential to achieve the long-sought-after monolithic integration of electronics and photonics. Notwithstanding the recent exciting developments in (Si)GeSn materials and devices, this family of semiconductors is still facing serious limitations that need to be addressed to enable reliable and scalable applications. The main outstanding challenges include the difficulty to grow high-crystalline quality layers and heterostructures at the desired content and lattice strain, preserve the material integrity during growth and throughout device processing steps, and control doping and defect density. In this presentation, I will discuss experimental protocols to control Sn segregation during the epitaxial growth of (Si)GeSn thin layers, heterostructures, and nanowires. The atomic-level properties immediately after growth and upon thermal annealing will be discussed based on 3-D atom probe tomography analyses. Insight into the stability of (Si)GeSn materials during post-growth processing will also be addressed.

Effect of valence electrons on the core level x-ray photoelectron spectra of 4d transition-metal oxide thin films

Jasnamol Pezhumkattil Palakkal (Advanced Epitaxy, Institute of Materials Physics, Georg-August-University of GÃ¶ttingen, Germany), **Pia Henning** (Georg-August-University of Gottingen), **Lambert Alff** (TU Darmstadt)

Keywords: Characterization, Fundamentals; Thin Film; Oxides; MBE

A final-state screening effect of charge carriers causes additional peaks in the x-ray photoelectron spectroscopy (XPS) spectra of electron-doped transition metal oxides (TMO) [1, 2]. These extra peaks are often contemplated as originating from other oxidation states of the TM cation. Lin et al. reported a theoretical calculation of the XPS spectra of d1 and electron-doped d0 TMO by comparing them with experimental results [1]. They suggested that such multiple peaks do not always originate from other cationic states but are intrinsic to the material. We prepared ultrathin films of partially oxidized Nb using e-beam-assisted molecular beam epitaxy. The samples were produced by varying the flow of oxygen from 0.00 to 0.30 SCCM (Samples: Nb0.00 to Nb0.30), which maintained the pressure of the growth chamber from 1x10-11 to 1.7x10-6 mbar, respectively. Before the XPS measurements, the films were in contact with air to purposefully introduce native oxide Nb2O5 [3] for reference spectral position. Starting from Nb0.00 (Nb0 & Nb5+) and fully oxidized Nb0.30 (Nb5+), we estimated the positions of satellite peaks for Nbx+ that were presumed as originating from final-state effect [1]. The final-state effect occurs when the photoelectron ejected during XPS leaves a core hole behind, which interacts with the valence electrons and alters the energy of valence electrons [1]. We found that the closeness of the valence band (VB) peak to the Fermi level (Îµf) and the number of electrons in the VB affect the appearance and intensity of this additional peak. Only the initial-state effect is exhibited by an oxide containing Nbx+ when there are no electrons present near the Îµf. However, when the lattice offers electrons to the VB close to Îµf due to defects, the binding energy of Nbx+ is decided not only by core-level energy but also the interaction of valence electrons with the core hole, which results in manifold peaks in the XPS spectra of Nb 3d at a lower binding energy than that of the core-level. We will also show Nb 3d XPS spectra of conducting perovskite SrNbO3 and insulating perovskite AgNbO3 to support this presumption further. We observed a similar effect when this experiment was repeated on Mo-based oxides. This presentation will discuss the final-state effect in the XPS spectra of Nb- and Mo-based TMO. References 1. Lin, C., et al., Phys.Rev.B, 2015. 92(3): p.035110. 2. Scanlon, D.O., et al., J.Phys.Chem.C, 2010. 114(10): p.4636-4645. 3. Halbritter, J., Appl.Phys.A., 1987. 43(1): p.1-28.

Invited Talk

Ken Jackson's Life and Work

Vincent Fratello (Quest Integrated, LLC), **Robert Feigelson** (Stanford University)

Keywords: Fundamentals, Ken Jackson Symposium

Professor Kenneth A. Jackson, a pioneer in the field of crystallization science, passed away January 7, 2022, at his home in Prescott Arizona at the age of 92. In the 1960â€™s, together with Bob Laudise, he helped found the American Association for Crystal Growth (AACG) and they both shared its first presidency. Prior to that, he was part of the organizing committee of the first ICCG in Boston. In 1998 he won the IOCG Frank Prize at ICCG-XII in Jerusalem. Kenâ€™s book â€œKinetic Processes: Crystal Growth, Diffusion, and Phase Transformations in Materialsâ€□ is widely used within the crystal growth community. In addition he was the third President of the Materials Research Society (MRS). Ken contributed many outstanding discoveries that have affected the entire area of crystal growth. His major scientific interests were the kinetic processes of crystal growth, the molecular theory of crystal growth, thin film growth and characterization, defect formation in crystals, ion beam processes, alloy crystallization, semiconductor processing, and molecular dynamics simulations of crystal growth. As grad students under Bruce Chalmers, Ken, Bill Tiller and John Rutter analyzed the mathematics of the diffusion process in the liquid ahead of a crystal growth interface and derived the equation for constitutional supercooling. This concept had an enormous influence on the field and laid the foundation for the field of shape stability of crystals during growth. Ken rationalized the crystallization behavior of inorganic and organic compounds in terms of the dimensionless entropy of melting, which is used as a scale for the ease of crystallization resulting in the Jackson "alpha factor" that determines the surface roughening of growth fronts. At Bell Labs Ken and John Hunt studied the question of where the nuclei come from to make the equiaxed zone in metal alloy castings and further studied dendritic growth and experimentally compared the calculated interface shapes, defining the three classes of dendrite microstructures based on the entropies of fusion of the components. Ken also pioneered computer simulation studies of atomic-scale processes during crystal growth, in collaboration with George Gilmer and Harry Leamy. They were able to generate excellent and enlightening images of surfaces below and above the surface roughening transition. At the University of Arizona, Kenâ€™s research group contributed new insight into nonequilibrium segregation during crystal growth, crystallization of silicon simulated using Monte Carlo modeling and nonequilibrium phase transformations. He also continued his interest in materials aspects of electronic packaging.

Invited Talk

Relating stress in thin films to the processes of crystal growth

Eric Chason (Brown U)

Keywords: Fundamentals; Thin Film; Nitrides, metals; Sputtering, VPE; Energy Materials, Optical Materials

A long history of measurements shows that residual stress in thin films is intimately connected to the kinetics of growth and morphological evolution. For instance, metal films that grow with tensile stress at low temperatures or high growth rates may develop compressive stress when grown at higher temperatures or lower growth rates. In addition, the stress may change with thickness so that the film is tensile in the early stages, when individual islands are coalescing, and then become compressive after the film has become continuous. We have developed a kinetic model that relates the stress to the underlying fundamental kinetic processes that control film growth including, deposition, surface diffusion and grain boundary formation. Examples are shown of how the model can analyze multiple sets of measurements to derive kinetic parameters that can predict the stress under different processing conditions. The model has been implemented as a user-friendly program that can be used by the thin film growth community to analyze their stress measurements.

Invited Talk

BCF Analysis of Azimuth Dependence of Step Dynamics

Gregory Brian Stephenson (Argonne National Laboratory), **Dongwei Xu** (Huazhong University of Science and Technology), **Carol Thompson** (Northern Illinois University), **Matthew J**. **Highland** (Argonne National Laboratory), **Jeffrey A**. **Eastman** (Argonne National Laboratory), **Weronika Walkosz** (Lake Forest College), **Peter Zapol** (Argonne National Laboratory), **Bo Shen** (Peking University)

Keywords: Fundamentals, Growth; Thin Film; Nitrides; VPE; UWBG/WBG Semiconductor; Energy Materials

We have been studying the dynamics of atomic steps on vicinal surfaces during OMVPE growth of GaN [1]. Here we present a Burton-Cabrera-Frank (BCF) type analysis for step, kink, and adatom dynamics on vicinal (0001) surfaces of GaN, which extends our previous work [2] by including the effect of step azimuth (the in-plane angle of the steps). The alpha/beta/alpha/beta stacking sequence of the basal planes produces half-unit-cell-height steps of alternating types that have different kinetics for adatom attachment. This leads to a variation in the steady-state fraction of surface covered by alpha or beta terraces as a function of growth or etching rate. We include a model for step transparency, in which adatoms can diffuse across steps if they detach before finding a kink site. Since the kink spacing depends on step azimuth, this introduces a specific azimuth dependence. Comparison of predictions with in situ surface X-ray scattering measurements [1,3] of the steady-state and dynamics of the alpha terrace fraction during OMVPE allows a determination of fundamental kinetic parameters for adatom attachment and diffusion. [1] Guangxu Ju et al., In-situ microbeam surface X-ray scattering reveals alternating step kinetics during crystal growth, Nature Communications 12, 1721 (2021). [2] Guangxu Ju et al., Burton-Cabrera-Frank theory for surfaces with alternating step types, Physical Review B 105, 054312 (2022). [3] Guangxu Ju et al., Crystal truncation rods from miscut surfaces with alternating terminations, Physical Review B 103, 125402 (2021).

Invited Talk

Evolution of Jackson-Hunt Diffusion theory and transition into 3D-dendritic morphology: An Overview

Narsingh Singh (University of Maryland Baltimore County), **Mona Chopra** (University of Maryland Baltimore County), **Martin Glicksman** (Florida Institute of Technology)

Keywords: Fundamentals, Growth; Bulk, 2D; Melt Growth; Nonlinear; Optical Materials

The diffusion theory developed by Jackson-Hunt and roughness parameter (ï□„S/R) parameter for eutectics have been key for developing facetted and non-faceted films and single crystals for RF and electronic systems. Eutectic alloys have been widely used for structural and soldering applications including turbine blades for variety of systems. In the early stage this theory was verified by using few transparent organic materials with very low roughness parameters. However, a large number of papers were published using variety of faceted-non faceted and faceted-faceted materials. The knowledge of interface breakdown in pre- and post-eutectics provides current status of variety of observed lamellar and rod morphologies. In this presentation we will discuss the validation of Jackson-Hunt model using organics and its evolution where thousands of papers have been published. This provided very important steps to develop industrially important materials for RF, products. Although eutectics have been used in variety of industrial applications, we will focus examples of facetted and non-faceted variety of organic and inorganic such as Al-Si dendrites and their pathway for developing variety of materials for electronic and optical applications.

Applying Kinetic Monte Carlo Modeling to Irregular Rod Eutectic Systems

Daniel Bentz ()

Keywords: Fundamentals, Growth, Modeling; Bulk; Novel, Silicon; Melt Growth, Solution Growth; Self Ordering; Optical Materials, Advanced Cathodes

The directional solidification of regular eutectic systems are relatively well understood via Jackson-Hunt theory. These are systems consisting of two solid phases growing from a single liquid phase with both of the solid-liquid interfaces above the roughing transition, i.e. growth is not impeded by surface nucleation. However, the growth of irregular eutectic systems, when one or both of the solid-liquid interfaces are faceted, is not. To gain insight into these systems, studies were performed on an analog, two component, lattice gas system of a regular solution solid in contact with an ideal liquid. The interaction potentials between the two components were assigned such that solid solution supported two separate solid phases. The composition of the liquid was set to support rod growth. The dynamics of the lattice gas models were handled by Kinetic Monte Carlo (KMC). Growth of rods was initiated from columns of pure A atoms embedded in a matrix of B atoms. These computational analog systems have the advantage of capturing the growth kinetics above and below the surface roughening transition. In a separate study, the surface roughening transition of a regular solution solid in contact with a ideal solution was determined using fluctuation dissipation theory, where the kinetic behavior of the interface is related to the characteristic time of fluctuations about an equilibrium position. Results of this study showed a sharp transition in the kinetic behavior of the interface as a function of Jackson's alpha factor. As a result of these two models, multiple irregular eutectic systems were explored and deviations corresponding to previous experimental studies were observed.

Invited Talk

Stress modulation via oscillations in emergent grain boundary phases during growth of polycrystalline thin films

Moneesh Upmanyu (Northeastern University), **Mengyuan Wang** (University of Science and Technology of China), **Hailong Wang** (Northeastern University)

Keywords: Fundamentals, Modeling; Thin Film

The quality and reliability of crystalline thin films is strongly influenced by stress and morphological evolution during their synthesis. In this talk, I will present our recent computational results that uncover a new mechanism for stress generation and relaxation during growth of polycrystalline thin films. Crystalline interfaces such as grain boundaries that terminate at the surfaces often undergo structural transitions. As a classical example, valleys or ridges form on the surfaces of (111) FCC thin films at tilt grain boundaries (GBs) that lower their energy by reorienting their misorientation axis along the <112> direction within the GB plane. Using atomistic deposition computations of bicrystalline copper thin films constrained to grow along the (111) direction, we find that the emergent GBs (eGBs) restructure under deposition fluxes and lead to formation of 2D islands in the vicinity of an elastically stressed <112> eGB phase (complexion) confined to nanoscale thick surface layers. Layer growth from these islands increases the phase thickness while atom insertion events at the eGBs that precede the growth of each layer destabilize the valleys and decrease the phase thickness. The oscillations in the eGB phase thickness during layer-by-layer film growth has ramifications for stress and morphological evolution during synthesis of wide range of polycrystalline thin films.

Invited Talk

Concentration-driven transition between classical and nonclassical modes in organic crystallization

Peter Vekilov (University of Houston), **Manasa Yerragunta** (University of Houston), **Akash Tiwari** (New York University), **Bart Kahr** (New York University), **Peter G. Vekilov** (University of Houston)

Keywords:

One of the most consequential assumptions of the classical crystal growth theories is the Szilard postulate, which states that molecules join a growing crystal individually. Myriad examples of classical crystallization by sequential addition of single molecules exist. Recent studies have documented numerous violations of the Szilard rule, whereby amorphous or crystalline precursors form in the solution and incorporate into a crystal surface contributing to a fast growth mode. The found transition to nonclassical crystal growth requires chemical modifications that range from solution pH and ionicity shifts to the addition of auxiliary compounds. Here we demonstrate that crystals of etioporphyrin I transition from classical to nonclassical growth driven only by increasing solute concentration. Etioporphyrin I crystals carry appealing optical and electronic properties due to their low symmetry. At moderate supersaturations, etioporphyrin I crystals grow classically by the association of solute molecules to dislocation-generated steps. At elevated supersaturations, numerous particles of size about 100 nm land on the crystal surface and contribute to a fast non-classical growth mode. These particles merge with the crystal lattice and transform into stacks of about 20 crystal layers, which then spread along the surface and coalesce with other layer stacks. Light scattering characterization of etioporphyrin I solutions reveals the presence of mesoscopic solute-rich clusters which exhibit the four signature behaviors of this phase: their average diameter, about 100 nm, is steady in time and independent of the solute concentration, their number increases exponentially with solute concentration, and the solute concentration, with which they equilibrate, correlates with the initial solute concentration. These properties of the clusters distinguish them from domains of other condensed phases, such as crystals or dense liquids. The size similarity between the clusters and the particles landing on the crystal surface suggests that the particles originate as mesoscopic solute rich clusters which may land on the surface while still liquid. Crystal quality assessment by polarized microscopy reveals that crystals grown nonclassically are of similar quality to those growing classically at low supersaturations. The observations with etioporphyrin I crystallization suggest that fast crystal growth may be achieved by transitioning to nonclassical growth mode’s without sacrificing crystal quality and utility.

Crystal Growth, Structure and Magnetism of Transition Metal â€œHobbyâ€ Crystals

Rylan Terry (Clemson University), **Ben Bell** (Clemson University), **Sydney Maddox** (Clemson University), **Joseph Kolis** (Clemson University)

Keywords: Characterization, Growth; Bulk; Oxides; Solution Growth; Magnetic

Whether pursuing vibrantly colored crystals for enjoyment or as new magnetic materials, classical transition metal containing coordination complexes are a favorite of hobbyists, professional crystal growers and magnetic scientists. Many vintage coordination compounds provide both beautiful colored crystals and intriguing physical properties. Sometimes compounds that are popular amongst hobby communities do not even have known structures or have never been magnetically characterized. An example of a material that bridges the gap between these two very different worlds is Cu(HCOO)2(H2O)2Â·2CO(NH2)2. In addition to forming large, beautiful blue blocks the compound contains very interesting magnetic characteristics. Small bridging ligands such as formate facilitate the magnetic exchange of open shell 3d transition metal ions such as Cu2+, Mn2+, Co2+, and Ni2+ and provide us with a path to investigate their quantum properties using bulk magnetic measurements and neutron scattering. Such measurements typically require large single crystals to provide optimal measurements. With the variety of possible bridging species available and versatility in which they may coordinate, it is possible to produce a wide range of novel 1D, 2D, or 3D coordinated species. This work will focus on the use of organic ligands such as urea that are capable of hydrogen bonding, to generate coupling between 1D chains and 2D layers, but also assist in single crystal growth. This talk will revisit the classical crystal chemistry of 3d transition metal complexes that are grown by hobbyists for their beauty, but also possess interesting magnetic properties.

Invited Talk

Impact of configurational entropy on point defect thermodynamics in silicon

Talid Sinno (University of Pennsylvania), **Jinping Luo** (Xi'an Jiaotong University), **Lijun Liu** (Xi'an Jiaotong University)

Keywords: Defects, Fundamentals, Modeling; Bulk; Silicon; Melt Growth; Semiconductor; Energy Materials

It has long been suggested that the familiar intrinsic point defects (vacancies and self-interstitials) encountered in crystals at low temperatures transform into extended domains characterized by a missing or excess atom compared to the same-sized region in the perfect crystal so that such â€œextended defectsâ€ may be viewed as droplet-like regions of enhanced or diminished density. Yet the implications of such a transformation, or whether it even occurs in crystalline Si, remain uncertain. To address this fundamental problem, here we consider a comprehensive thermodynamic analysis of the thermodynamics of vacancy and self-interstitial formation over a broad temperature range based on thermodynamic integration with a particular focus on entropic contributions. In cooled liquids, it is well known that the form of the intermolecular potential can greatly influence the configurational entropy and, correspondingly, we analyze several empirical Si potentials to determine how the potential influences both the temperature dependence of the configurational entropy, as well as the enthalpy and entropy of defect formation. We show that the configurational entropy associated with point defects increases significantly upon heating, consistent with the existence of extended defects. Moreover, each type of defect species gives a significantly different contribution to the configurational entropy at elevated temperature and to a qualitive difference in the temperature dependence of the entropy of defect formation in the extended defect regime. We discuss some potential consequences of these thermodynamic changes of defect formation on the temperature dependence of diffusion in heated crystals.

Crystallization pathways and interfacial drivers for the formation of hierarchical architectures

Maria Sushko (Pacific Northwest National Laboratory (PNNL)), **Lili Liu** (PNNL), **Duo Song** (PNNL)

Keywords: Fundamentals; Low Dimensional, 2D; Oxides; Solution Growth; Optical Materials, Quantum Materials

The development of structural hierarchy on various length scales during crystallization process is ubiquitous in biological systems and is also observed in synthetic nanomaterials. The driving forces for the formations of complex architectures range from local interfacial interactions, that modify interfacial speciation, local supersaturation, and nucleation barriers, to macroscopic interparticle forces. Although it is enticing to interpret the formation of hierarchical architectures as the assembly of independently nucleated building blocks, often crystallization pathways follow monomer-by-monomer addition with structural complexity arising from interfacial chemical coupling and strongly correlated fluctuation dynamics in the electric double layers. Here, the mechanism of the development of structural hierarchy through heterogeneous nucleation, coupled interfacial nucleation and assembly, and oriented attachment of independently nucleated particles is discussed. The emphasis is made on the discussion of the underlying interfacial forces and chemical coupling that drives crystallization pathways towards the formation of structural hierarchy.

Investigation of Synthesis Growth and Characterization of Single Crystal of 2-Methyl Benzimidazole and 4-Aminobenzoic Acid for Photonic Applications

Ramki Chakaravarthy (Saveetha Engineering College), **Sowmiya Kumar**, **Gunasekaran B**

Keywords: Fundamentals; Bulk; Novel; Solution Growth; Nonlinear; Optical Materials

In this work, 2-Methyl benzimidazole and 4-Amino benzoic acid single crystal was obtain from slow evaporation technique at room temperature using ethanol as a solvent. The grown crystal (C15 H17N3O3) was subjected to single crystal X-ray diffraction (XRD) and confirmed that the crystal belongs to orthorhombic crystal system with non-centrosymmetric space group P 21/n. The vibrational modes of different functional groups were clearly identified using FT-IR spectral analysis. The lower cut off wavelength of the crystal is around 315nm and optical energy band gap is 3.67eV. The powdered sample of crystal was taken for simultaneous TG-DTA analysis in nitrogen atmosphere. And the TG data shows that the material is stable up to 134Â°C and the corresponding weight loss of about 76%. The DTA data indicates the sharp endothermic peak appears in 110Â°C,137Â°C,254Â°C. The laser damage threshold (LDT) energy has been measured using an Nd: YAG laser. The nonlinear refractive index (n2), absorption coefficient (b) and third-order nonlinear susceptibility (Ï‡(3)) were studied using Z-scan technique with a continuous wave (CW) laser of 632.8 nm.

Invited Talk

Freestanding semiconductor nanomembranes: from materials to devices

Abderraouf Boucherif (Université de Sherbrooke)

Keywords:

TBD

Invited Talk

All-epitaxial growth of orientation-patterned GaAs and GaP engineered nonlinear optical crystals

Peter Schunemann (BAE Systems, Inc.)

Keywords: Devices, Growth; III-Vs (Traditional); MBE, VPE; Nonlinear; Optical Materials

III-V compound semiconductors â€“ particularly GaAs and GaPâ€“ have very attractive properties for nonlinear opical frequency conversion. Both are non-centrosymmetric, and their highly polarizable covalent bonds result in high nonlinear coefficients (d14= 94 pm/V for GaAs, 35 pm/V for GaP). They exhibit broad transparency ranges which extend deep into the mid-infrared, high thermal conductivites, higher purity levels, and very low absorption losses when grown from the vapor phase. Mature, industrial bulk and epitaxial crystal growth technology exists for both materials, and their robust mechanical properties favor fabrication and polishing of devices with high laser damage thresholds, Because they are not birefringent, there is no way to achieve phase matching in bulk devices. (Form birefringence has been used to achieve phase matching in waveguide devices, but these offer impractically low output powers and efficiencies.) However, quasi-phase-matching is an option if a viable process for producing periodic domains of alternating polarity at relevant cohenernce lengths can be achieved in these materials. Unlike ferroelectric oxides, whose periodic domain structure is created by electric-field poling, the QPM grating structure of compound semiconductors is achieved using polar-on-nonpolar molecular beam epitaxy (MBE) whereby a polar GaAs (GaP) epi-layer is grown on a on a thin, lattice-matched non-polar Ge (Si) layer with an orientation that is inverted with respect to the GaAs (GaP) substrate. (Actually both the inverted and non-inverted polarities nucleate with equal probability on the silicon layer, but under the proper temperature conditions and the use of off-cut (100) GaP substrates - 4Â° towards <111B> - the domains with the same polarity as the substrate form a pyramidal morphology which self-annihilates, leaving a single-domain inverted layer after ~ 1200Ã… of growth.) The inverted layer is then photolithographically patterned with the desired grating period and alternate domains are etched back to the original substrate surface. Both orientations are then re-grown, first by MBE (to a thickness of 1-2 ï□m), then by hydride vapor phase epitaxy7 (HVPE) at rates of ~ 100ï□m/hr to produce thick QPM layers (â‰¥ 1000 ï□m) for in-plane laser pumping. In this presentation we describe detailed processing techniques used to produce engineered QPM grating structures in orientation-patterned GaAs (OP-GaAs) and GaP (OP-GaP), resulting in numerous highly efficient, broadly-tunable mid-infrared laser sources for a wide range of spectroscopy applications.

Growth of AlInP by Dynamic-Hydride Vapor Phase Epitaxy for Optoelectronic Devices

Jacob Boyer (National Renewable Energy Laboratory), **Kevin Schulte** (National Renewable Energy Laboratory), **Aaron Ptak** (National Renewable Energy Laboratory), **John Simon** (National Renewable Energy Laboratory)

Keywords: Devices, Growth; Thin Film; III-Vs (Traditional); VPE; Optoelectronic/Photovoltaic; Energy Materials

We demonstrate AlInP growth by dynamic-hydride vapor phase epitaxy (D-HVPE) and integrate this material as a passivating window layer to increase the efficiency of photovoltaic devices. D-HVPE is an epitaxial growth technique with the potential for high-throughput, low-cost deposition of a variety of III-V optoelectronic devices [1]. Until recently, AlInP , which has the widest bandgap of As/P materials at the GaAs lattice constant, had not been integrated in D HVPE-grown devices due to difficulties with Al precursors in the HVPE environment. AlCl reacts readily with quartz reactor hardware and outcompetes deposition of other group III species, making mixed cation materials, like AlInP, effectively impossible to grow in HVPE. We and others have since addressed these barriers in initial studies of Al(Ga)InP growth [2], [3], [4]. These successes employ an Al-source that generates AlCl3 within a colder, ex-situ source held at ~ 400Â°C. Unlike AlCl, AlCl3 has much lower reactivity with quartz and resists predeposition of Al at temperatures used in typical HVPE processes. The presence of uncracked PH3 also contributes to these successes by enabling a hydride-enhanced growth, a kinetically controlled growth mechanism that overrides the differences in thermodynamic potential for growth between InCl and AlCl3. As a result, we can control AlInP growth and realize growth rates >25 Î¼m/h , similar to other HVPE-grown materials [5]. We develop AlInP growth to achieve films with acceptable smoothness, n-type doping, and impurity levels (O and Si) for integration within solar cell devices. AlInP-passivated solar cells show a >1 mA/cm2 increase in photocurrent relative to GaInP-passivated solar cells, which is expected due to the reduction in parasitic absorption between these materials, while all other performance metrics remain the same. We also demonstrate a AlInP-passivated GaAs solar with an open circuit voltage of 1.10 V, which is effectively equivalent to that of state-of-the-art GaAs solar cells produced by OMVPE [6]. [1] J. Simon, K. Schulte, K. Horowitz, T. Remo, D. Young, and A. Ptak, â€œIII-V-Based Optoelectronics with Low-Cost Dynamic Hydride Vapor Phase Epitaxy,â€� Crystals, vol. 9, no. 1, p. 3, Dec. 2018, doi: 10.3390/cryst9010003. [2] K. L. Schulte et al., â€œGrowth of AlGaAs, AlInP, and AlGaInP by Hydride Vapor Phase Epitaxy,â€� ACS Appl. Energy Mater., vol. 2, no. 12, pp. 8405â€“8410, Dec. 2019, doi: 10.1021/acsaem.9b02080. [3] J. T. Boyer, K. L. Schulte, M. R. Young, A. J. Ptak, and J. Simon, â€œAlInPâ€�passivated IIIâ€“V solar cells grown by dynamic hydride vaporâ€�phase epitaxy,â€� Progress in Photovoltaics, vol. 31, no. 3, pp. 230â€“236, Mar. 2023, doi: 10.1002/pip.3629. [4] Y. Shoji, R. Oshima, K. Makita, A. Ubukata, and T. Sugaya, â€œ28.3% Efficient IIIâ€“V Tandem Solar Cells Fabricated Using a Tripleâ€�Chamber Hydride Vapor Phase Epitaxy System,â€� Solar RRL, p. 2100948, Dec. 2021, doi: 10.1002/solr.202100948. [5] W. Metaferia, K. L. Schulte, J. Simon, S. Johnston, and A. J. Ptak, â€œGallium arsenide solar cells grown at rates exceeding 300 Âµm hâˆ'1 by hydride vapor phase epitaxy,â€� Nat Commun, vol. 10, no. 1, p. 3361, Dec. 2019, doi: 10.1038 /s41467-019-11341-3. [6] S.-T. Hwang et al., â€œBandgap grading and Al0.3Ga0.7As heterojunction emitter for highly efficient GaAs-based solar cells,â€� Solar Energy Materials and Solar Cells, vol. 155, pp. 264â €“272, Oct. 2016, doi: 10.1016/j.solmat.2016.06.009.

Imaging dislocation networks formed by using defect filter layers in the growth of GaSb on GaAs.

Ganesh Balakrishnan (University of New Mexico), **Darryl Shima** (University of New Mexico), **Thomas Rotter** (University of New Mexico), **Fatih Ince** (University of New Mexico)

Keywords: Characterization, Defects, Growth; Thin Film; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials, Quantum Materials

The majority of the antimonide devices are grown on GaSb substrates. These include detectors, lasers, thermophotovoltaic devices and transistors. However, the ability to grow such devices on a GaAs substrate could have significant benefits, including larger substrate sizes, semi-insulating substrates and reduced surface defect density. An added factor is the economics of growing on GaAs which is a much more established substrate technology and costs considerably less when compared to GaSb. The interfacial misfit dislocation growth mode allows us to realize high quality metamorphic GaSb on GaAs. This growth mode is superior to other metamorphic approaches such as step graded buffers due to the spontaneous relaxation of the GaSb layer on the GaAs substrate thus resulting in significant reduction in buffer thickness. It has resulted in ~ 108 dislocations/cm2 with instantaneous relaxation for 0.5 Î¼m of GaSb grown on GaAs. This is achieved by the formation of a highly periodic misfit dislocation array between the GaSb and GaAs layers that almost fully accommodates the mismatch.[1] Several publications by various authors have shown cross-section transmission electron micrograph (X-TEM) analysis and selective area diffraction analysis of the growth, showing complete and spontaneous relaxation of the GaSb epilayers.[1, 2] In this work we include AlSb based defect filter layers immediately after the GaSb/GaAs interface to bend residual dislocations. The mismatch between AlSb (ao AlSb = 6.13 Ã…) and GaSb (ao GaSb = 6.09 Ã…) results in compressive strain at the growth interface which causes the dislocations to bend at this interface. The bent dislocations at the AlSb/GaSb interface form a secondary network that appear as a mesh in plan view transmission electron micrographs. The dislocations interact with each other, resulting in significant annihilation and a much reduced threading dislocation density of ~ 107 dislocations/cm2. The presentation will provide an extensive TEM based analysis of the GaSb/GaAs misfit dislocation interface and the plan view analysis of dislocation annihilation in AlSb/GaSb defect filter layers.

Invited Talk

MOCVD growth of InAs/InP quantum dots for C-band to near 2 Âµm emission

Qiang Li (Cardiff University)

Keywords: Devices, Growth; Low Dimensional, Thin Film; III-Vs (Traditional), Silicon; CVD, VPE; Narrow Semiconductor; Optical Materials

To date, 1300 nm O-band quantum dot (QD) lasers have demonstrated superior performance to their quantum well counterparts. The zero-dimensional dot gain medium and delta-function-like density of states lead to lower threshold current density and reduced temperature sensitivity. Benefiting from the strong resilience of quantum dot lasers to crystal defects and their insensitivity to external optical feedback, integrated InAs/GaAs QD lasers on silicon substrates by direct epitaxy are now envisaged as one of the most promising solutions to bring on-chip light sources to silicon photonics platforms. This has sparked a growing interest in developing InAs/InP QDs for lasers operating at 1550 nm C-band and longer wavelength optical communication bands. However, the moderate lattice mismatch and the increased complexity in growing the dot/cladding matrix in these materials present some unique challenges in achieving in-plane symmetric quantum dots of high optical quality. In this talk, I will present MOCVD development of InAs/InAlGaAs QDs for C-band lasers on both InP and silicon substrates. The impact of the pre-layer, growth interruption and the dot capping process will be discussed. Electrically injected QD lasers and their integration on the silicon platform will also be presented.

Invited Talk

Monolithically Integrated III-V Lasers for Silicon Photonics

Ting Wang (Institute of Physics, Chinese Academy of Sciences)

Keywords: Characterization, Defects, Devices, Growth; Low Dimensional; III-Vs (Traditional), Silicon; MBE; Narrow Semiconductor

Realizing monolithic integration of III-V lasers and silicon photonic components on single silicon wafer is recognized as a long-standing challenge for ultradense photonic integration, which can provide considerable economical, energy-efficient and foundry-scalable onchip light sources. Here, we demonstrate embedded InAs/GaAs quantum dot (QD) lasers directly grown on trenched silicon-on-insulator (SOI) substrate, enabling monolithic integration with buttcoupled silicon waveguides. By utilizing the patterned grating structures inside pre-defined SOI trenches and unique epitaxial method via hybrid molecular beam epitaxy (MBE), high-performance embedded InAs QD lasers with monolithically out-coupled silicon waveguide are achieved on such template. By resolving the epitaxy and fabrication challenges in such monolithic integrated architecture, embedded III-V lasers on SOI with continuous-wave lasing up to 85 Â°C are obtained with estimated coupling efficiency of approximately -6.7 dB.

Real-time, In-situ Flux Monitoring: A Revolutionary New Development in Solid-Source Molecular Beam Epitaxy

James Gupta (University of Ottawa), **Zbigniew Wasilewski** (University of Waterloo), **Laura Burchell** (Queen's University, Canada), **Leslie Lebrun** (National Research Council of Canada), **John Weber** (National Research Council of Canada, Canada)

Keywords: Fundamentals, Growth, in-situ monitoring, Technology/Equipment; applicable to all materials systems; MBE

We present a revolutionary new capability for real-time, in-situ monitoring of both group-III and group-V fluxes during solid-source molecular beam epitaxial growth. The technique is enabled by a custom MBE system design employing flux-monitoring ports deliberately positioned to monitor fluxes bypassing the substrate manipulator during growth. Bayard-Alpert ionization gauges in these ports provide real-time flux monitoring for the group-III and As fluxes, while a quadrupole mass spectrometer is used to monitor the 121Sb flux. We present compelling examples of the high signal:noise achieved during the growth of test structures on GaSb and InAs substrates, as well as during the growth of InGaAsSb/Al(In)GaAsSb laser diodes on GaSb.

InP Nano-Ridge Engineering for III-V device integration on silicon substrates

Reynald Alcotte (IMEC), **Yves Mols** (IMEC), **Peter Swekis** (IMEC), **Guillaume Boccardi** (IMEC), **Robert Langer** (IMEC), **Bernardette Kunert** (IMEC)

Keywords: Growth; Selective area growth; III-Vs (Traditional); CVD; III-V semiconductors; For RF and optoelectronic

The integration of III-V semiconductors on silicon platform has the great potential to combine analog functions with Si-based technologies (CMOS or Silicon Photonics), especially InP-related optoelectronic and RF devices, but it requires cheap integration of InP and related alloys to Si substrates with high crystal quality. The monolithic integration is a way to avoid expensive III-V substrates and enable large wafer-scale production. However, lattice mismatch and thermal expansion coefficient difference between III-V and Si induces defect formation. Nano-ridge engineering (NRE) is an innovative approach to integrate III-V on Si without needing thick strain-relaxed buffers for defects reduction. Starting from selective area growth (SAG) of III-V in trench-patterned Si substrates to ensure efficient aspect ratio trapping (ART) of defects, the heteroepitaxial growth continues outside of the pattern to increase the III-V volume. A nano-ridge (NR) with a specific shape is engineered for a particular III-V device on 300mm Si wafers in a cost-efficient way while profiting from a mature industrial tool park. In this paper, we explore NRE of InP grown by metal-organic vapor phase epitaxy (MOVPE) in trenches with widths varying from 80nm to 500nm and an aspect ratio (AR) from 4.75 to 1.25. Different seed materials such as InP and InGaAs were used to study the growth mechanism and defects formation of threading dislocations (TD) and planar defects (PD). The samples were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron channeling contrast imaging (ECCI) techniques. In comparison to GaAs or InGaAs NR, we observed from TEM images that different defect formation mechanism is dominating in InP NRE. Although ART of TD is very efficient, a high density of PD is generated at a certain trench filling height depending on the trench width. An ECCI defect study of InP NRs applying an InGaAs or InP seed indicates for narrow trenches (AR = 4.75) a comparable threading dislocation density (TDD) of 1x107cm-2 whereas the planar defects density (PDD) per NR length is two times lower (0.4Âµm-1) with an InGaAs seed. Furthermore, the impact of the Si substrate treatment before III-V nucleation was investigated for InP on an InP seed. A TEM inspection reveals an InP polarity change when applying a tertiarybutylarsine (TBAs) during cooling down from the substrate bake temperature which also impacts PD orientation. This study points out that the key criterium to enable integration of InP on Si is to control the planar defect formation.

Invited Talk

Defect Evolution and Mg Segregation in implanted GaN using Ultra-High-Pressure Annealing

Mark Goorsky (UCLA), **Yekan Steven Wang** (UCLA), **Michael Liao** (Naval Research Laboratory), **Kenny Huynh** (UCLA), **James Tweedie** (Adroit Materials), **Ramon Collazo** (NCSU), **Dolar Khachariya** (Adroit Materials), **Zlatko Sitar** (NCSU)

Keywords: Characterization, Defects; Thin Film; Nitrides; Implantation; UWBG/WBG Semiconductor; Energy Materials

Vertical GaN power devices have emerged to become promising candidates for next-generation high power applications due to superior material properties such as high breakdown voltage, low on-resistance, and high mobility compared to devices based on Si and SiC. GaN-based p-n junction switching devices enable higher voltage power with significantly higher efficiencies while adding advantages of systems with reduced size and weight. A technological limitation of GaN, however, has been the inability to achieve high p-type doping in a planar, vertical device. Here, we will focus on recent developments to achieve high p-type efficiency though ion implantation, novel high temperature post-implant annealing schemes, and the importance of defects and morphology in native substrates and epitaxial layers. In particular, annealing ta temperatures of 1300 C and above removes the strain induced by the implantation process. However, annealing at 1300 C leads to the formation of Mg-containing inverted domain structures, but annealing at 1400 C does not lead to the formation of the inverted domains and actually dissolves such domains if the 1400 C step follows annealing at lower temperatures which did form the domains. Results from this work are expected to help achieve higher activation efficiency of p-type doping for devices including vertical GaN device structures. This research was supported through the ARPA-E PNDIODES program under contract DE-AR0001116 at UCLA. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Ofï¬□ce of Science User Facility operated for the DOE Ofï¬□ce of Science by Argonne National Laboratory under contract no. DE-AC02-06CH11357.

Stress induced van der Waals lift-off of 4-inch GaN grown on two-dimensional BN by metal organic chemical vapor deposition

Michael Snure (Air Force Research Laboratory), **Eric Blanton** (KBR), **Timothy Vogt** (Agnitron Technology), **Andrei Osinsky** (Agnitron Technology), **Nicholas Glavin**

Keywords: Growth, Technology/Equipment; Thin Film; Nitrides; CVD; UWBG/WBG Semiconductor; Electronics Integration

Epitaxial lift-off (ELO) of high quality GaN layers allows for integration with a wide variety of materials enabling improved performance, reduced costs, and development of new electronics. Of the ELO technologies, van der Waals (vdW) based lift-off offers great promise but is still in the early stages of development and has yet to demonstrate the scale and yield of other ELO technologies. Here we discuss the potential of this process?s scalability, speed, and yield moving from laboratory scale to 4-inch lift-off of GaN films using a 2D BN van der Waals (vdW) buffer layer. Compared to other potential vdW buffer layers, like graphene and MoS2, sp2 bonded BN is interesting due to its atomically flat and smooth surface, high temperature and chemical stability, excellent insulating and dielectric properties, and ability to be grown uniformly over large areas by commercial techniques such as metal organic chemical vapor deposition (MOCVD). Key challenges to GaN growth, including nucleation and strain will be covered with the goal of achieving high quality films that can be easily lifted off and transferred. Since, the BN layer acts as the growth template and mechanical release layer, both the quality and adhesion of the GaN layer are corelated with the BN morphology and uniformity. Detailed characterization mapping demonstrates excellent BN uniformity, which translates into growth of high quality GaN verified by a suite of structural, optical and surface characterization techniques. Characterization of the interfaces with scanning transmission electron microscopy and electron energy loss spectroscopy reveals abrupt chemically distinct interfaces between the sapphire, BN, and AlN/GaN layers essential for efficient lift-off. To induce mechanical lift-off, Ni spalling has been used to efficiently lift-off and transfer full 4-inch GaN layers, individual devices, and selectively defined areas.

Single-Crystalline Layer-Transferred III-N Films for Flexible Piezoelectric Sensors in Extreme Environment Applications

Jae-Hyun Ryou (University of Houston), **Nam-In Kim** (University of Houston), **Muhammad Aqib** (University of Houston), **Miad Yarali**

Keywords: Devices; Thin Film; Nitrides; CVD, MBE; UWBG/WBG Semiconductor; Energy Materials, Sustainable Materials

Piezoelectric sensors are increasingly being adopted in various industries, including automotive, plant, and biomedical, owing to their advantages such as high sensitivity, fast response time, ease of manufacturing, reliable operation, lightweight, and low power consumption. However, one of the key characteristics required for extended applications is flexibility. For instance, flexible sensors attached to membranes can be used to measure gas pressure in a closed gas inlet or outlet network. While flexible piezoelectric sensors made from various materials have been developed for typical situations, there is a shortage of materials that can operate at ultra-high temperatures above 500Â°C. Lead zirconate titanate (PZT), the most common piezoelectric material, has high piezoelectric coefficients, but its low Curie temperature limits its operation at high temperatures. Similarly, piezoelectric materials based on zinc oxide (ZnO) and polyvinylidene fluoride (PVDF) face challenges due to the increase in oxygen vacancies and low melting point, respectively, as the temperature increases. To address this issue, III-N thin films are being explored for high-temperature operations owing to their wide bandgap energy, spontaneous polarization, and low electrical conductivity. Single-crystalline gallium nitride (GaN) and aluminum nitride (AlN) piezoelectric thin films have exhibited excellent output voltage up to 400 and 900 Â°C, respectively, indicating outstanding sensitivity, quick response time, chemical and mechanical long-term stability, high thermal resistance, and excellent biocompatibility. In this study, we developed and demonstrated single-crystalline piezoelectric GaN and AlN flexible thin film for gas pressure sensing at very high temperatures. The crack-free AlN epitaxial layers were epitaxially grown and the flexible III-N thin-film-based sensors were fabricated using a layer transfer process. The sensors exhibited excellent crystalline quality without secondary phases or defects. A single sensor was attached to the membrane with a fitting tool and placed in an electric furnace. The working condition of the sensor was controlled from low to high temperature with different gas pressures, and its long-term stability was evaluated. Simulations were performed to support the results at each temperature and pressure. Additionally, we compared the sensing performance after exposing the sensor to radiation. Overall, the flexible III-N piezoelectric sensors developed in this study offer high durability under harsh conditions and can be used in various applications such as aerospace, nuclear plant, and defense.

Defect Elimination in N-Polar GaN Nanostructures on Si

Alexana Roshko (National Institute of Standards and Technology, Boulder, Colorado), **Matthew Brubaker** (National Institute of Standards and Technology), **Kristine Bertness** (National Institute of Standards and Technology)

Keywords: Characterization, Defects, Devices, Growth; selected area, Thin Film; Nitrides; MBE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Ordered arrays of N-polar GaN nanostructures on Si are desired for low-cost, large-scale manufacturing of easily integrable devices. A promising route for obtaining these nanostructures is selective area growth (SAG), which precludes many of the issues associated with etched structures. Unfortunately, the metal-rich conditions required for N-polar nitride growth on Si by plasma assisted molecular beam epitaxy (PAMBE) typically result in eutectic formation and concomitant inversion domains (IDs) and voids.[1] These defects can disrupt growth, particularly at heterostructure interfaces, so their elimination is desirable. We have investigated the prevalence of defects in N-polar GaN nanowires and nanofins grown by metal-rich PAMBE SAG on Si(111) substrates. The samples consisted of AlN followed by GaN buffer layers, patterned silicon nitride masks and subsequent GaN nanostructures; all growths were N-polar. The sample polarity and defect structures were determined from scanning transmission electron microscopy (STEM) imaging, and ID formation was monitored with photoluminescence (PL). Remarkably, while the AlN and GaN buffer layers contained substantial numbers of threading dislocations (TDs), IDs and voids, these defects did not propagate into the SAG nanostructures. Similar to TDs, which typically annihilate at sidewalls near the base of SAG nanowires, IDs and voids have associated interface/surface energies which are driving forces for their elimination.[2] This combined with the more rapid growth of N-polar material compared to metal-polar material likely accounts for their observed termination at the regrowth interface. In several nanowires, IDs were observed to initiate at or close to the regrowth interface, and PL peaks associated with recombination at IDBs (at 3.45 and 3.457 eV) were found in these samples. STEM X-ray analysis revealed no detectable contamination at the base of these IDs. However, the intensity of the PL peaks was directly correlated with the Ga collection area: increasing both with decreasing NW diameter and with increasing NW pitch, suggesting excess Ga in the SAG aperture promotes ID formation. Consistent with this model, IDB peak intensities were significantly lower for fins, which have a reduced Ga collection area relative to that of NWs with similar widths and spacings. These results suggest a path to obtain defect free N-Polar GaN nanostructures on Si. References [1] A. Roshko, et al., Phys. Stat. Sol. B 1900611 (2019); A. Roshko, et al., Jpn. J. Appl. Phys. 58, SC1050 (2019). A. Roshko, et al., Crystals 8, 366 (2018). [2] J.E. Northrup, J. Neugebauer and L.T. Romano, Phys. Rev. Lett. 77, 1, 103 (1996).

Invited Talk

GaN on GaN Epigrowth Using Chemically Pure Hydride Vapor Phase Epitaxy (HVPE)

Jacob Leach (Kyma Technolgies), **Kevin Udwary** (Kyma Technologies), **Heather Splawn** (Kyma Technologies)

Keywords: Growth, Technology/Equipment; 2D; Nitrides; VPE; UWBG/WBG Semiconductor; Energy Materials, Power Electronics

Heteroepitaxial GaN-based power electronics have made significant headway in recent years against Si-based devices for low voltage (<1200V) applications. Homoepitaxial GaN devices have great potential to compete directly with SiC-based devices in medium voltage (>1200V) applications, if issues related to the bulk GaN substrates and challenges in growing thick epilayers can be managed. The epitaxy challenges stem from issues related to growing thick (10-50 microns) homoepitaxial GaN layers with controlled values of Nd-Na in the 10^15-10^16 range considering the high values of carbon (an acceptor, Na) associated with films grown by the incumbent MOCVD process. We will outline our efforts at developing thick, high quality, lightly doped GaN epilayers using HVPE, a carbon-free process, for medium voltage power electronics devices.

Piezoelectric Single-Crystalline Flexible GaN Thin Film for Stress Hormone Detection from Sweat

Jae-Hyun Ryou (University of Houston), **Nam-In Kim** (University of Houston), **Asad Ali** (University of Houston)

Keywords: Devices; Nitrides; CVD; UWBG/WBG Semiconductor

Wearable and skin-attachable sensors are increasingly important in biomedical applications, especially in personal healthcare monitoring. Stress has a significant impact on a person's health and can lead to the release of cortisol and adrenaline into bodily fluids. It is important to monitor cortisol levels in these fluids to maintain healthy conditions, as long-term stress can lead to chronic illnesses. However, the current stress sensors have limitations, and they are susceptible to interference from other ions and off-target analytes. Furthermore, transistor-based sensors require an external electric supply to monitor cortisol. Recent studies have explored the use of organic electrochemical transistors and field-effect transistor-based cortisol sensors with cortisol antibody embedding technology to create a sensing layer. However, these sensors are also susceptible to interference from other ions and off-target analytes, and they require an external electric supply. A solution to this problem is to functionalize piezoelectric-based quartz crystal microbalance (QCM)-type sensors with a cortisol monoclonal antibody. QCM-type sensors have a certain resonant frequency, and the force that the target substance exerts on the sensing layer is caused by its mass, which alters the initial resonant frequency in the negative direction. QCM-type sensors have outstanding response times and selectivity, and a higher initial frequency can pick up on low cortisol levels. In this study, a III-N thin film-based QCM-type sensor for the detection of cortisol was designed and shown to be single-crystalline and free of second phase or defects by X-ray diffraction analysis. The sensor was exposed to controlled cortisol solutions, and the concentration affected the resonance frequency. The selectivity of the sensor was confirmed using diluted versions of several hormones. For comparison, synthetic bodily fluid and actual sweat were both taken from volunteers who had participated in both exercise and sauna sessions. Overall, wearable and skin-attachable sensors are becoming increasingly important in biomedical applications. A III-N thin film-based QCM-type sensor with a cortisol monoclonal antibody shows promise for the detection of cortisol with outstanding response times, selectivity, and a higher initial frequency that can pick up on low cortisol levels.

Optimization of ZnGeN2/GaN Quantum Wells for Green LEDs

Moira K. Miller (Colorado School of Mines), **Anthony D. Rice** (National Renewable Energy Laboratory), **David R. Diercks** (Colorado School of Mines), **Adele Tamboli**, **Brooks Tellekamp** (National Renewable Energy Laboratory)

Keywords: Characterization, Devices, Growth; Thin Film; III-Vs (Traditional), Nitrides, Novel; MBE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Newly theorized hybrid II-IV-N2/III-N heterostructures, based on current commercialized (In,Ga)N light-emitting diodes (LEDs), are predicted to significantly advance the design space of highly efficient optoelectronics in the visible spectrum, specifically in the green to amber regions where LED efficiencies are orders of magnitude lower than other colors. Yet, there are few epitaxial studies of II-IV-N2 materials. ZnGeN2, a ternary analogue of the wide bandgap material GaN, is explored as a potential green-to- amber emitter which can be integrated into existing GaN LED heterostructures due to structural similarity. Cation-ordered ZnGeN2 has a theoretical band gap pf 3.4 eV, which is expected to be reduced with cation disorder. ZnGeN2 is wurtzite when disordered, and is structurally and electronically similar to GaN, possessing a lattice mismatch of ~0.8%. Past work by this group has demonstrated epitaxial growth of ZnGeN2 on GaN and AlN via molecular beam epitaxy (MBE) [1,2]. Here we present the first growth of well-defined quantum wells (QW) of ZnGeN2 within GaN by nitrogen plasma-assisted MBE, including successful five-layer multiple quantum well (MQW) structures. Detailed structural and elemental analysis of the heterostructures was performed, including X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (STEM-EDS), and atom probe tomography (APT). These methods demonstrate high-quality and abrupt interfaces in the heterostructures, even after multiple repeating heterointerfaces. Through changes in growth methodology, we also demonstrate methods to improve unintentional incorporations, including associated improvements in structural quality. We then include reports of a full LED stack growth, including n- and p-type GaN for carrier injection, an InGaN/GaN short-period superlattice, the ZnGeN2/GaN active region, and an AlGaN electron blocking layer. Together, this data demonstrates both the promise of heteroepitaxially integrated hybrid ternary/binary nitride systems along with the challenges associated with growing such systems, including an outlook on methods to improve the materials and devices. References [1] M. B. Tellekamp et al. Heteroepitaxial integration of ZnGeN2 on GaN buffers using molecular beam epitaxy. Crys. Growth Des. 2020; 20, 3, 1868â€“1875. [2] M. B. Tellekamp et al. Heteroepitaxial ZnGeN2 on AlN: Growth, Structure, and Optical Properties. Crys. Growth Des. 2022; 22, 2, 1270â€“1275.

Strain Accumulation and Relaxation in AlN Film on Si (111) Substrate: A Consideration on Crack Formation in Epitaxial Growth of Ultrawide-Bandgap Semiconductor Films

Muhammad Aqib (University of Houston), **Mina Moradnia** (University of Houston), **Sara Pouladi** (University of Houston), **Jae-Hyun Ryou** (University of Houston)

Keywords: Growth; Thin Film; Nitrides; CVD, MBE, Sputtering, VPE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials, Sustainable Materials

Aluminum nitride (AlN) with ultrawide bandgap energy in the family of Group III-nitride (III-N) semiconductor materials, exhibits a great technological potential for high-power high-voltage electronics, piezoelectric sensing and energy harvesting, and deep UV photonics. It is desirable to epitaxially grow relatively thick AlN films and device structures on a large-area economical Si substrate for manufacturing cost reduction, monolithic integration of AlN and Si, and an easy layer-transfer process. However, the epitaxial growth of a crack-free thick layer of AlN on a Si substrate is very challenging. For example, cracks typically formed in the AlN layer with thickness exceeding ~200-300 nm in most chemical vapor epitaxy carried out higher than 1000 Â°C and in any AlN layers thicker than ~1 Î¼m. While the experimental results are described in terms of mismatches in lattice constants and thermal expansion coefficients between AlN and Si, detailed calculations to estimate the conditions of crack formation have not been performed. In the present study, we employ Griffith theory of brittle fracture and Mathews-Brakeslee theory of misfit dislocations in the estimation of strain accumulation and relaxation for the epitaxial growth of AlN on Si (111) substrate. Strain energy associated with the growth of AlN on Si was calculated using different models based on solid mechanics for multiple crystallographic orientations. The strain energy increases with the thickness of the layers, as expected, but slightly decreases with increasing temperature. Then, the relationship between strain energy and cleavage energy in thick AlN layers grown on Si substrates was investigated. It is noted that one can grow a crack-free layer of AlN on Si substrate as long as the strain energy is lower than that of cleavage energy. On the other hand, if cleavage energy is less than strain energy it ultimately leads to crack formation in the layer. Also, the strain energy and formation of misfit dislocations play a critical role in the cleavage formation in AlN growth. After the detailed calculations, we then compared the estimated theoretical results with experimental results reported in the literature. We also suggest a possible pathway to grow crack-free AlN thick layers on Si (111) substrate using new buffer layers between AlN and Si. These findings have important implications for the design and fabrication of AlN-based devices and highlight the need for careful control of the growth conditions to minimize strain and improve the quality of AlN films on Si substrates.

Invited Talk

Revealing the Alternating Step Kinetics during Nitride Growth by OMVPE

Guangxu Ju (Peking University), **Dongwei Xu** (Huazhong University of Science and Technology), **Carol Thompson** (Northern Illinois University), **M. J. Highland** (Argonne National Laboratory), **J. A. Eastman** (Argonne National Laboratory), **Weronika Walkosz** (Lake Forest College), **P. Zapol** (Argonne National Laboratory), **B. Shen** (Peking University), **G. B. Stephenson** (Argonne National Laboratory)

Keywords: Characterization, Defects, Fundamentals, Growth, Technology/Equipment; Low Dimensional, Thin Film; III-Vs (Traditional), Nitrides; Sputtering, VPE; UWBG/WBG Semiconductor; Energy Materials, Sustainable Materials

Understanding the kinetics of incorporating atoms at steps on vicinal surfaces is crucial for growing epitaxial films of GaN and incorporating alloying elements like indium. On vicinal {0001} surfaces of GaN, the alternating A and B step structures and kinetics result in distinctive growth morphologies. Furthermore, it has been suggested that the attachment kinetics of atoms at atomic-scale steps significantly influences the incorporation of indium, and theoretical predictions indicate that composition inhomogeneities can contribute to lower internal quantum efficiency for higher indium fractions [1]. Improving our understanding of these mechanisms can help us control the incorporation of indium and other alloying elements, leading to better device performance. However, identifying the A or B structure of steps is challenging, making it difficult to determine which structure has faster adatom attachment kinetics. Our recent in-situ studies of GaN homoepitaxy using organo-metallic vapor phase epitaxy (OMVPE) under step-flow conditions have shown that microbeam surface x-ray scattering can unambiguously determine differences in the attachment kinetics at A and B steps [2]. Analysis of the surface scattering [3] combined with an extension [4] of the classic Burton-Cabrera-Frank (BCF) theory allowed us to obtain the first direct information on step attachment rate constants in this system. In this presentation, I will also discuss our recent experiments to determine the influence of the step azimuth on the alternating dynamics of GaN (0001) steps, for comparison to predictions from our BCF theory. Going forward, we plan to extend this work to address the incorporation of indium during Ga1-xInxN growth by OMVPE. [1] Matthias Auf der Maur et al., Efficiency Drop in Green InGaN/GaN Light Emitting Diodes: The Role of Random Alloy Fluctuations, Phys. Rev. Lett. 116, 027401 (2016). [2] Guangxu Ju et al., In-situ microbeam surface X-ray scattering reveals alternating step kinetics during crystal growth, Nature Communications, 12(1): 0-1721 (2021). [3] Guangxu Ju et al., Crystal truncation rods from miscut surfaces with alternating terminations, Physical Review B, 103: 125402-1-125402-14 (2021). [4] Guangxu Ju et al., Burton-Cabrera-Frank theory for surfaces with alternating step types, Physical Review B, 105(5): 054312-1-054312-20 (2022). I would be deeply appreciative if you could kindly consider extending an invitation for me to present my research at the conference. Thank you for your time and consideration.

Micro-Electroluminescence and -Photoluminescence of Hexagonal Hillocks in UVC LEDs

James Loveless (North Carolina State University), **Ronny Kirste** (North Carolina State University), **Baxter Moody** (North Carolina State University), **Pramod Reddy** (North Carolina State University), **Shashwat Rathkanthiwar** (North Carolina State University), **Will Mecouch** (Adroit Materials), **Dolar Khachariya** (Adroit Materials), **Jack Almeter** (North Carolina State University), **Cristyan Quiñones-García** (North Carolina State University), **Ramon Collazo** (North Carolina State University), **Zlatko Sitar** (North Carolina State University)

Keywords: Characterization, Defects, Devices; Thin Film; III-Vs (Traditional), Nitrides; CVD, VPE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Light emitting diodes with emission in the UVC range are widely envisioned for disinfection applications. Through the development and use of native AlN substrates, highly efficient and reliable devices have been developed, heralding a new paradigm in UVC optoelectronic development. A common defect in epitaxial layers grown on AlN substrates is the 3D growth of hexagonal hillocks with sizes on the order of a few microns. Despite their near ubiquitous presence, only a handful of studies have been performed on these defects, and even fewer on their effect on semiconductor device performance. The consensus is that these defects act as current leakage sites which is deleterious to device performance. There is still much that is not understood, especially their effects on lifetime and reliability of devices. A better understanding of these defects is needed in order to develop techniques and methods to reduce or eliminate their formation, or otherwise circumvent negative impacts to device performance. In this study, a luminescence mapping technique is utilized to investigate hillocks, in conjunction with traditional electrical and optical characterization. Electroluminescence and photoluminescence from hillocks and surrounding areas is mapped and analyzed as a function of current and device operation time. These measurements directly verify that hillocks act as parallel diodes with a lower potential barrier owing to higher gallium incorporation. Other than an earlier turn-on voltage for the hillocks, electrical measurements indicate remarkably similar electrical properties between the hillock areas and the LED as a whole. The hillock related emissions diminish in comparison to bulk LED emission, indicating a lower radiative efficiency in hillock regions. This is because unwanted impurities will have a higher incorporation rate like gallium, causing higher instances of non-radiative recombination. Electrical and optical properties are also investigated as a function of total operation time to gain understanding into degradation mechanisms in UVC LEDs. This work provides insights into these important defects that will contribute in ultimate efforts to increase the efficiency and reliability of UVC LEDs and other devices developed on AlN substrates.

On the solubility of boron nitride in supercritical ammonia-sodium solutions

Jacob Dooley (Lehigh University), **Nathan Stoddard** (Lehigh University), **Kai Landskron** (Lehigh University), **Siddha Pimputkar** (Lehigh University)

Keywords: Growth; Bulk; Nitrides; Solution Growth; UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Boron nitride (BN) is an ultra-wide bandgap semiconductor with multiple observed polymorphs. Amongst these, the hexagonal polymorph (h-BN) has received considerable interest for its optoelectronic, quantum optic, and electronic properties when used as an insulating 2D material layer or substrate, while the cubic polymorph (c-BN) exhibits extreme properties as a super hard material and promising intrinsic electronic and thermal properties which could enable even higher power and higher efficiency power electronic devices compared to currently explored ultra-wide bandgap materials. Synthesis of large-area, bulk BN has been challenging in large part due to the strong covalent bonds requiring high synthesis temperatures. State-of-the-art, thick BN is grown using high-pressure, high-temperature (HPHT) anvil systems resulting in high-quality h-BN and c-BN on the scale of a few-mm diameter size flakes. Nonetheless, scaling of this technique to yield inch-scale boules is required to further develop BN-based devices and no clear pathway to achieve this has yet been identified or demonstrated. Flux-based synthesis approaches have successfully demonstrated growth of bulk h-BN as a film that grows on the interface between the flux and ambient gases effectively limiting achievable thicknesses. An alternative synthesis technique is required to enable large, bulk boules and a solvothermal process is desirable as it can result in a reduction of the required growth temperature and pressure thereby enabling scalability and industrialization. This talk will lay the foundation for the application of the ammonothermal method to the synthesis of BN from solution. The ammonothermal method utilizes supercritical ammonia (held at ~ 1,000â€”3,000 atm and ~ 450â€” 900 Â°C) as a solvent that can dissolve and crystallize matter using a temperature gradient, assuming a temperature-dependent solubility of the solute is demonstrated. This method has been successfully used to grow gallium nitride (GaN) single crystal, >2-inch diameter boules on an industrial scale. This study reports on the initial investigation of the solubility of boron (B) in supercritical ammonia solutions containing sodium as the mineralizer. Solubility of B into solution was determined on gravimetric bases by heating an ammonia-filled nickel-chromium superalloy autoclave to multiple isothermal soak temperatures between 450 and 600 Â°C for 2 days and then quickly cooling the system. Cubic BN material was used as the feedstock and was measured before and after exposure to the supercritical ammonia solution. The resulting temperature-dependent solubility curve will be discussed and contrasted to the established solubility curves for GaN.

RF-MBE Growth of GaN on ScAlMgO4 Substrate

Tsutomu Araki (Ritsumeikan University), **Yuuchi Wada** (Ritsumeikan University), **Yuuya Kuroda** (Ritsumeikan University), **Seiya Kayamoto** (Ritsumeikan University), **Naoki Goto** (Ritsumeikan University), **Momoko Deura** (Ritsumeikan University), **Takashi Fuji** (Ritsumeikan University), **Y. Shiraishi** (Fukuda Crystal Laboratory Co., Ltd.), **Tsuguo Fukuda** (Fukuda Crystal Laboratory Co., Ltd.)

Keywords: Growth; Thin Film; Nitrides; MBE; UWBG/WBG Semiconductor; Energy Materials

ScAlMgO4 (SAM) has recently attracted attention as a substrate for nitride semiconductor crystal growth. SAM substrates have a smaller lattice mismatch with GaN (1.8%) than with sapphire or Si, and are also lattice-matched with In0.17Ga0.83N. Furthermore, the difference in thermal expansion coefficient with GaN is also small. Interesting results have been obtained so far, including improved crystal quality of GaN and InGaN grown on SAM substrates, exfoliation of GaN thin films using the cleavage property of SAM substrates, and improved InGaN MQW emission properties using lattice-matched InGaN templates. Recently, it has become possible to grow dislocation-free 2-inch SAM crystals, which is applied to the fabrication of GaN freestanding substrates. On the other hand, under high-temperature growth atmosphere such as MOCVD and HVPE, Mg desorbs from the surface of SAM substrates. Therefore, we investigated the direct growth of nitride semiconductors on SAM substrates using RF-MBE, which enables crystal growth at temperatures several hundred degrees lower than those of the MOCVD under ultra-high vacuum conditions. First, the effect of the terrace width of the SAM substrate on the direct growth of GaN was examined. GaN thin films were grown on SAM substrates with average terrace widths;160-440 nm, i.e., Î¸off=0.1-0.3Â°. The SAM substrates were all atomically flat and had a well-defined step-and-terrace structure with a step height of 0.8 nm. The SAM substrate with the largest terrace width yielded a flat continuous wurtzite (WZ)-GaN film, while the SAM substrate with the smallest terrace width showed a mixture of WZ-GaN islands and metastable zincblende (ZB)-GaN islands. Regardless of the terrace width of the SAM substrate, WZ-GaN grew to an initial thickness of 5-15 nm, then, stacking faults and ZB phase were found to be mixed in some of the surfaces. Increasing the terrace width (decreasing the step density) had the effect of reducing the coalescing interface density of the WZ-GaN islands and suppressing ZB inclusion. Based on these results, uniform GaN film growth on a 2-inch (0001) SAM substrate was also achieved using the RF-MBE method. GaN growth (400 nm thick) was performed at 700Â°C. The RHEED pattern after growth showed streaks, suggesting that flat GaN was grown. The FWHMs of the rocking curves are about 600 arcsec for (002) GaN and about 1300 arcsec for (302) GaN.

Conduction mechanism in Mg-doped compositionally graded AlGaN: the role of polarization field and point defects

Shashwat Rathkanthiwar (North Carolina State University), **Pramod Reddy**, **Dolar Khachariya**, **Pegah Bagheri**, **Cristyan Quiñones-Garcia**, **James Loveless** (North Carolina State University), **Masahiro Kamiyama** (North Carolina State University), **Yasutomo Kajikawa** (Shimane University), **Rafael Dalmau** (Hexatech Inc.), **Baxter Moody** (Adroit Materials Inc.), **Seiji Mita** (Adroit Materials Inc.), **Ronny Kirste** (Adroit Materials Inc.), **Ramon Collazo** (North Carolina State University), **Zlatko Sitar** (North Carolina State University)

Keywords: Characterization, Defects, Growth; Thin Film; Nitrides; CVD; UWBG/WBG Semiconductor; Optical Materials

P-type compositionally graded AlGaN films exhibit superior conductivity as compared to the constant composition p-AlGaN films and have, therefore, garnered significant interest as a hole injection layer in UV lasers and light-emitting diodes. The mechanism behind this improvement in conductivity remains controversial. In this talk, the conduction mechanisms in Mg-doped, compositionally graded AlGaN films will be discussed. The compositional grading was found to significantly alter the electrical nature of the Mg-doped films exhibiting characteristic features of the impurity band conduction mechanism for a range of Mg doping concentrations from 2x1018 to 1.5x1019 cm-3. While the resistivity was found to have a shallow temperature dependence in a wide temperature range of 200-700K, the Hall coefficient exhibited anomalous sign reversal from positive to negative as the temperature was lowered. The electrical results are analyzed based on a two-band transport mechanism where the free hole conduction in the valence band is favored at high temperatures and hopping conduction in the impurity band dominates at low temperatures. The sign reversal of the Hall coefficient is attributed to fundamentally different Hall scattering factors for impurity and valence band conduction. A model is proposed to study the impact of the polarization field and compensating point defects on the carrier transport mechanism. It is hypothesized that the polarization field in the graded AlGaN film acts as a perturbation to the electronic state of Mg. This spreads the carrier wavefunction leading to impurity band transport via the Anderson transition. This hypothesis was validated by a systematic set of experiments involving a variation in the composition gradient, Mg doping level, and point defect concentration in the AlGaN layers. A clear transition between the valence band and impurity band conduction mechanisms was observed. The transition temperature depended strongly on the compositional gradient and concentration of point defects. It was found that steeper gradients significantly enhance the probability of phonon-assisted hopping transitions between Mg atoms regardless of the doping level. Charged compensating point defects were found to suppress the impact of the polarization field by reducing the overlap integral needed for impurity band formation. While this study bolsters the mechanistic understanding of the conductivity enhancement in p-type compositionally graded AlGaN films, it also points out that controlling compensation is as important as in conventional doping. Record-high p-conductivity of 0.7 â„¦-1cm-1 is demonstrated in high Al-content AlGaN.

Invited Talk

Green Solar Wafers for High-Efficiency Solar Cells Produced by Epitaxy

Frank Siebke (NexWafe GmbH), **Maxi Richter** (NexWafe GmbH), **Giuliano Vescovi** (NexWafe GmbH), **Klaus Wachtmann** (NexWafe GmbH), **Bernd Stannowski** (Helmholtz-Zentrum Berlin)

Keywords: Technology/Equipment; Bulk; Silicon; CVD; Energy Materials

While solar photovoltaics (PV) produce no greenhouse gas (GHG) emissions during operation, significant GHG emissions are associated with their production and transportation. Silicon wafers are the most energy-intensive component of a PV module. While conventional wafer production contains several high-temperature processes, such as polysilicon production and ingot pulling, NexWafe offers a cleaner, more efficient, and cheaper solution based on epitaxy. We have developed high-throughput processes and equipment for kerfless mass manufacturing of silicon wafers for photovoltaics. By using anodic etching technology for the fabrication of porous Si layers on large-area single-crystal Si substrates for subsequent epitaxial deposition of silicon wafers by APCVD, we produced n-type silicon wafers with 1 Ohm cm resistivity and minority carrier lifetimes exceeding 2.5 ms in average. HJT solar cells have been made at Helmholtz-Zentrum Berlin on our EpiNexâ„¢ wafers and open circuit voltage VOC exceeding 740 mV have been demonstrated. PL mapping of the solar cells show the influence of crystal defects on the solar cell performance. The results show that carbon emissions in wafer manufacturing can be reduced by more than 70% when compared with the conventional Czochralski process in regions that rely on coal-based electricity without sacrificing solar cell efficiency. NexWafeâ€™s innovative and unique technology creates the opportunity to profitably manufacture ultra-low-carbon green solar wafers.

Invited Talk

MBE growth of single and polycrystalline CdTe and CdSeTe for photovoltaic applications

Alexander Goldstone (Sivananthan Laboratories Inc.), **Ramesh Dhere** (Sivananthan Laboratories Inc.), **Christoph Grein** (Sivananthan Laboratories Inc.), **Paul Boieriu** (Sivananthan Laboratories Inc.), **Sivalingam Sivananthan**

Keywords: Growth; Thin Film; II-VI; MBE; Narrow Semiconductor; Energy Materials, Optical Materials, Sustainable Materials

Polycrystalline CdTe-based thin film solar cells are at the forefront of commercial thin film photovoltaic devices with production levels approaching 20 GW per year. There have been considerable research efforts to enhance the performance of these devices, which have resulted in efficiencies reaching 22.1%. However, the open circuit voltage (VOC) remains stuck below 900 mV, limiting further progress. Prior work on single crystal devices has demonstrated VOC over 1000 mV. There is a need to understand the factors limiting VOC of polycrystalline devices by developing a better understanding of single crystal devices. Molecular beam epitaxy (MBE)-grown single crystal CdTe and CdSexTe1-x layers are ideally suited for such studies. Sivananthan Laboratories Inc. performs fundamental research in the MBE crystal growth of II-VI materials and has developed the growth of single crystal CdTe on Si substrates. The epitaxial growth of CdTe on Si has been highly optimized for crystallinity and surface quality, demonstrating x-ray rocking curve FWHM as low as 50 arcsec. These substrates have been successfully used for the development of large area, high-performance infrared devices. Sivananthan laboratories is working on a joint effort, the CdTe Accelerator Consortium (CTAC)* funded by the DOE, with other photovoltaic groups, to improve the device performance of polycrystalline CdTe devices to achieve their true potential. One of the major identified issues that limits performance is the low activation of dopants such as arsenic, which is well below 10%. In single crystal CdTe, arsenic activation over 50% is achievable with hole concentrations > 1x1016 cm-3. We are developing MBE processes to achieve high As activation in crystalline CdTe layers. We will systematically introduce grain boundaries in MBE-grown CdTe layers by epitaxial growth on polycrystalline templates from CTAC partners and study the effects of grain boundaries on the doping properties of polycrystalline layers. We will introduce impurities such as Cl in the crystalline and polycrystalline CdTe layers grown by MBE to understand their effects on doping and develop mechanisms to achieve high As activation. We are also working on molecular dynamics simulations of MBE processes for CdTe growth with As incorporation to develop a fundamental understanding of As doping in CdTe and CdSexTe1-x layers.

Optimizing Oxygen Reduction Reaction Efficiency through Templated Synthesis and Crystallographic Orientation Control of Transition Metals within Graphitic Nanofibers

Sivasankara Rao Ede (University of California Irvine), **David Kisailus** (University California Irvine)

Keywords: Characterization, Fundamentals; Nanofibers; Metal nanofibers; Electrospinning; Electrical conductivity; Energy Materials

Reducing oxygen is a crucial process in fuel cell operation, and improving the efficiency of this process can lead to eco-friendly energy generation from hydrogen fuel and air. However, using expensive Pt as a catalyst has limited the practical application of fuel cells. To address this issue, researchers have investigated cost-effective catalysts to replace Pt. It has been found that Pt with {111} crystal planes show superior ORR activity, whereas Pt with {110} crystal planes show enhanced activity when combined with Ni (PtNi3). The crystal plane-dependent ORR activity of transition metals, such as Mn, Fe, Co, Ni, etc., has not been studied until now. In this study, we prepared ORR catalysts with dominantly {111} or {110} crystal planes by varying the compositional ratio between two transition metals and using polymeric templates. These templates were subsequently processed into graphitic-based nanofibers using electrospinning and annealing processes. The as-synthesized catalysts showed good activity compared to commercial Pt/C catalysts. This research provides a fundamental understanding of how these parameters affect the crystal growth of transition metals. This opens up new possibilities for designing cost-effective catalysts for several electrochemical applications.

Invited Talk

Room-Temperature Growth, Ferroelastic Domains and Optoelectronic Properties of Halide Perovskite CH3NH3PbX3 (X = I, Br and Cl) and CsPbBr3 Single Crystals

Maryam Bari (Simon Fraser University), **Alexei A**. **Bokov** (Simon Fraser University), **Zuo**-**Guang Ye** (Simon Fraser University)

Keywords: Characterization, Growth; Solution Growth; Sustainable Materials

Halide perovskite single crystals form an ideal platform for investigating their inherent nature, such as structural, optical, photophysical, and photochemical properties because of their low defect concentration, high purity, and absence of grain boundaries. They exhibit superior optoelectronic performance and higher intrinsic/environmental stability compared to their polycrystalline counterparts, which would allow us to gain better fundamental understanding of their unique optoelectronic properties and explore their potential in photovoltaic and optoelectronic applications. Previously, inverse temperature crystallization (ITC) was used to grow halide perovskite crystals at high temperatures (ï‚» 100 ï‚°C). Here, we develop an effective synthetic technique by which the organic-inorganic hybrid halide perovskites CH3NH3PbX3 (X= I, Br and Cl) and all-inorganic halide perovskites CsPbBr3 are grown in polar solvents at room temperature (except for CH3NH3PbI3 grown at 45 ï‚°C) in a relatively short time. A constant supersaturation during the crystal growth is created to produce large single crystals, which is achieved during room temperature crystallization (RTC) through controlled solvent evaporation. The crystal structural analysis, steady-state absorption, photoluminescence, and charge-transport properties demonstrate excellent long-term stability (over 2 years) of the RTC-grown CH3NH3PbX3 (X= Br, Cl) and CsPbBr3 crystals against environmental degradation and moisture. Interestingly, the charge-transport characteristics and trap densities obtained for the RTC-grown crystals are comparable to those of the single crystals grown by the previous methods. In particular, the RTC-grown MAPbI3 crystal exhibits an ultra-high carrier mobility Î¼ of 410 cm2V-1s-1 and an ultra-long diffusion length LD of 10.75 Î¼m, suggesting that it could be a promising material for high-performance optoelectronic devices. In addition, the characteristic twin domains of these crystals are investigated by polarized light microscopy, and their crystal structures and phase transitions are accurately determined at wide range of temperature (80 K - 500 K). This work provides a novel and effective route to grow halide perovskite single crystals, and a better understanding of their physical properties, contributing to the acceleration of the development of crystals-based optoelectronic devices with superior performance and enhanced stability.

Invited Talk

Overview of hydride vapor phase epitaxy development for affordable III-V solar cells at AIST

Ryuji Oshima (National Institute of Advanced Industrial Science and Technology), **Yasushi Shoji** (National Institute of Advanced Industrial Science and Technology), **Kikuo Makita** (National Institute of Advanced Industrial Science and Technology), **Akinori Ubukata** (Taiyo Nippon Sanso Corporation), **Shuuichi Koseki** (Taiyo Nippon Sanso Corporation), **Takeyoshi Sugaya** (National Institute of Advanced Industrial Science and Technology)

Keywords: Devices, Growth; Thin Film; III-Vs (Traditional); VPE; Energy Materials

III-V multijunction solar cells have demonstrated potential for exceptionally high conversion efficiency. These technologies can open new applications, such as use in mobility and transportation systems in addition to the applications already in use today. However, one obstacle for implementing such solar cells is their high manufacturing cost. Hydride vapor phase epitaxy (HVPE) has recently emerged as a low-cost alternative to current fabrication processes of III-V solar cells owing to their fast growth feature using cheap metal chlorides. In this paper, we highlight the latest development of triple-chamber HVPE system (Taiyo Nippon Sanso, H260) for solar cell fabrications. Our HVPE reactor includes two growth chambers and one preparation chamber and abrupt heterointerfaces can be achieved by quickly shifting the susceptor between each chamber [1]. However, growing Al-containing materials via HVPE is inherently challenging because of the reaction of AlCl with the quartz reactor. In our reactor, AlCl3 was dominantly generated by the reaction of HCl with Al metal at 500 Â°C, while GaCl and InCl were generated at 700 Â°C. Consequently, we have presented the conversion efficiency (h) = 28.3% for GaInP/GaAs dual-junction solar cells grown with AlGaInP passivation layers [2]. Moreover, many efforts have been made to achieve fast growth rates while maintaining the solar cell performance. Regarding GaAs solar cells, the EL2 trap is well known to deteriorate device performance. The DLTS revealed that suppressing the thermal decomposition of AsH3 in the hot-wall reactor was effective for achieving fast growth with a lower V/III-input ratio and reducing the EL2 trap density at a given growth rate. The GaAs solar cells with improved growth condition exhibited almost no considerable cell parameter deterioration at up to 297 Î¼m/h. As a result, h = 24.0% with an open-circuit voltage (Voc) of 1.04 V was achieved at 200 Î¼m/h [3]. Contrary, the performance of GaInP solar cells was greatly affected by the CuPtB atomic ordering. Transmission electron diffraction revealed that the degree of atomic ordering became smaller with increasing the growth rates and almost disappeared at 117 Î¼m/h. The h = 16.3% with Voc = 1.39 V and h = 15.2% with Voc = 1.42 V were obtained for 28 Î¼m/h (1.88 eV) and 117 Î¼m/h (1.91 eV), respectively. [1] R. Oshima et al., J. Photovolt. 9, 154 (2019). [2] Y. Shoji et al., Solar RRL 6, 2100948 (2022). [3] R. Oshima et al., Crystals, 13, 370 (2023).

27% Efficient GaAs Solar Cells Grown on Acoustically Spalled Substrates for Lower Cost III-V Photovoltaics

Kevin Schulte (National Renewable Energy Laboratory), **Steve W. Johnston** (National Renewable Energy Laboratory), **Anna K. Braun** (Colorado School of Mines), **Jacob T. Boyer** (National Renewable Energy Laboratory), **Anica E. Neumann** (Colorado School of Mines), **William E. McMahon** (National Renewable Energy Laboratory), **Michelle Young** (National Renewable Energy Laboratory), **Pablo Coll** (Crystal Sonic Inc.), **Mariana I. Bertoni** (Arizona State University), **Emily L. Warren** (National Renewable Energy Laboratory), **Myles A. Steiner** (National Renewable Energy Laboratory)

Keywords: Characterization, Defects, Devices, Growth; Thin Film; III-Vs (Traditional); VPE; Energy Materials

We report the growth of high-efficiency GaAs solar cells by organometallic vapor phase epitaxy on non-flat substrate surfaces created by acoustic spalling, or â€œSonic Lift-offâ€� (SLO). SLO coupled with reuse is a potentially low-cost source of III-V epitaxial growth substrates, but surface facets formed during the SLO process can impact the performance of subsequently-grown devices. We study how the spalled surface morphology impacts device performance, finding that non-linear shunts can form in regions where the surface contains facets with 2-3 Âµm peak-to-valley height. These defects reduce the device efficiency via a reduction in the open-circuit voltage, despite quantum efficiency measurements that suggest that the bulk material quality is only slightly affected by the surface roughness. We present evidence from electrical device measurements and structural analyses that these shunts form at regions of non-conformal coating of the epitaxial layers over spalling-related surface features. We hypothesize that localized Schottky diodes form in these areas during device processing at points where the front contact grid-lines directly contact the p-type base of the n-on-p diode structure. We demonstrate that these defects can be mitigated or eliminated by planarizing the surface using wet chemical etching and/or growth. We study how material and dopant choices impact whether or not smoothing of faceted regions occurs during growth, leading to the development of effective planarization conditions for SLO substrates. Using a combination of etching and growth planarization, we demonstrate 0.25 cm2 devices with 27.0% photovoltaic conversion efficiency under the one-sun AM1.5G spectrum grown on an acoustically spalled substrate. These results show that the growth of high performance III-V devices is possible on rougher, non-traditional substrates that offer the potential for reduced cost.

GaAs/AlGaAs Photodetector Arrays for Soft X-ray Beam Position Monitoring

Jingze Zhao (Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook, NY 11794), **Kevin Kucharczyk** (Stony Brook University), **Jinghe Liu** (Stony Brook University), **Dmitri Donetski** (Stony Brook University), **Boris Podobedov** (NSLS II, Brookhaven National Laboratory, Upton, NY)

Keywords: Devices; Bulk; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials

Photoemission-based metal blade X-ray beam position monitors (XBPMs) are routinely utilized at the front ends of hard x-ray beamlines. In soft X-ray range (photon energies < 2 keV) photocurrents generated from metals are significantly reduced and the blades have to be inserted deeper into the beam producing significant wavefront distortions which become unacceptable in coherent soft-Xray beamlines. In order to support high resolution for coherent soft x-ray imaging in synchrotron beamlines the stability and positions of electron and photon beams have to monitored with non-invasive methods. With thermalization of the absorbed photon energy in the internal photoeffect semiconductor detectors produce significantly greater number of photoelectrons per X-ray photon offering higher responsivity in the soft X-ray range compared to that of metals. We proposed to install GaAs photodetector arrays in a halo of the soft X-ray beam for the beam position monitoring without imposing wavefront distortions [1]. Such detectors should be able to operate under beam power densities reaching 20 W/mm2 resulting in photocurrent densities of several hundred A/cm2 and elevated temperature which varies along the photodiode array length due to the beam intensity profile. In this work we proposed the AlGaAs/GaAs photodiode heterostructures where the X-ray responsivity is limited to the GaAs depletion region while AlGaAs graded composition layers block the transport of electrons generated primarily by soft X-ray photons in the p-type region near the surface as well as that for holes generated by higher energy harmonics penetrating deeper into the n-type substrate and reaching the pn junction by diffusion. This approach is aimed at the reduction of temperature dependence of the array responsivity in X-ray range for higher accuracy of determination of the beam center position. The heterostructures were grown by MBE. Details of the heterostructure design and characterization results will be presented. Authors are grateful for the support of the Accelerator & Detector Research Program of the Scientific User Facilities division, Office of Basic Energy Sciences, Office of Science of the U.S. Department of Energy (DOE). This research used beamlines 4-ID (ISR) and 23-ID-1 (CSX) of the NSLS-II, a DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DESC0012704. [1]. High power density soft x-ray GaAs photodiodes with tailored spectral response, D. Donetski, K. Kucharczyk, J. Liu, R. Lutchman1, S. Hulbert, C. Mazzoli, C. Nelson and B. Podobedov, Semicond. Sci. and Technol., 37, 085024 (2022).

Invited Talk

Molecular Insights into the Interactions between Antifreeze Proteins and Ice

Amish Patel (University of Pennsylvania), **Aniket Thosar** (University of Pennsylvania), **Yusheng Cai** (University of Pennsylvania), **Zachariah Vicars** (University of Pennsylvania), **Jeongmoon Choi** (University of Pennsylvania)

Keywords: Fundamentals, Growth, Modeling; Bulk; Melt Growth

Antifreeze proteins (AFPs) enable diverse organisms to survive frigid polar environments by preferentially binding ice crystals within their bodily fluids and passivating them. The ability of AFPs to perform one of the most challenging molecular recognition tasks in all of biology â€“ distinguishing between two different phases of water â€“ has long been a source of amazement and intrigue; not only are there no chemical differences to leverage, the structural differences between water and ice are also subtle. In addition to binding ice, AFPs must also resist engulfment by ice, and their ability to do so can influence their thermal hysteresis activity. Thus, AFPs must have certain regions that preferentially interact with ice and facilitate binding as well as other regions that interact unfavorably with ice (relative to water) and resist engulfment. Which AFP regions facilitate their binding to ice and which molecular characteristics enable them to subsequently resist engulfment? Moreover, how do these characteristics influence the AFP thermal hysteresis activity? To answer these questions, we combine molecular simulations with enhanced sampling techniques. We find that larger AFPs are better able to resist engulfment than smaller ones and that naturally occurring AFPs have evolved to optimally resist engulfment. By uncovering the molecular basis for AFP activity, we hope that our work will facilitate the engineering of novel AFPs with superior function.

Invited Talk

Crystal growth impedance from boundary layer transport, conformational interconversion, and dimerization kinetics

Baron Peters (University of Illinois at Urbana-Champaign), **Armin Shayesteh Zadeh**

Keywords: Fundamentals

Some crystal grow by exclusively incorporating one conformer or by exclusively incorporating pre-formed dimers. If the conformational interconversion rate (or the dimerization rate) is slow compared to the growth unit incorporation rate, then the kinetics of conformational interconversion (or dimerization) may impede the growth kinetics. We model these effects to quantify the degree of crystal growth impedance in mixed-suspension-mixed-product-removal reactors and for transport through a boundary layer to the growing crystals. Our analysis reveals simple expressions and dimensionless variables that can be used to anticipate when and how severely the kinetics of conformer interconversion and/or dimer formation will impact the growth kinetics. Finally, we use the model predictions to assess the impact of conformer interconversion kinetics in earlier experimental and computational reports.

Invited Talk

Reshaping and diffusion of metallic nanocrystals

Jim Evans (Iowa State University and Ames National Laboratory USDOE), **King Lai** (Fritz Haber Institut), **Yong Han** (Iowa State University), **Da-Jiang Liu** (Ames National Laboratory USDOE)

Keywords: Modeling; nanocrystal; metals; Sintering, Solution Growth, VPE; catalysis; catalysis, plasmonics

Metallic nanocrystals (NCs) can be synthesized either by solution-phase reduction of precursors (and possible transfer to supports), or by direct vapor deposition onto substrates. Advances in solution-phase synthesis allow exquisite control of shape to form nanocubes, octahedra, etc. which optimize performance in applications to catalysis, plasmonics, etc. However such shapes are intrinsically metastable and relax back to equilibrium, thereby degrading performance. Thus, we have developed predictive atomistic-level stochastic modeling for reshaping of fcc metal NCs mediated by surface diffusion. Kinetic Monte Carlo simulation of the model successfully assesses shape stability. Deeper insight into the kinetics of this reshaping process, which involves nucleation and growth of new 2D layers on outer facets, is provided by additional master equation and coarse-grained analysis. Similar methodology is applied to analyze the size-dependence of the diffusion of facetted NCs across supports revealing a fundamental failure of traditional mean-field analysis of NC diffusivity. See: J. Chem. Phys. 158 (2023) 104102; ACS Nano 14 (2020) 8551; Nanoscale 11 (2019) 17506; Chem. Rev. 119 (2019) 6670.

Invited Talk

Investigation of in-liquid ordering mediated transformations in Al-Sc via ab initio molecular dynamics and unsupervised learning

Deep Choudhari (New Mexico Institute of Mining and Technology), **Bhaskar S Majumdar** (New Mexico Institute of Mining and Technology), **Hunter Wilkinson** (New Mexico Institute of Mining and Technology)

Keywords: Fundamentals, Modeling; Metals and Alloys; Solidification

Scandium is well known to produce grain refinement in Al-based alloys, and its potency is generally attributed to intermetallic Al3Sc formation within liquid phase. However, the influence of Sc atoms and Al3Sc on the local structure of the surrounding melt, and subsequent nucleation remains unclear. Towards that end, we have probed structural changes in three bulk compositions, i.e., Al-xSc (x = 0, 0.4, 1.0 at.%), and near liquid-Al/Al3Sc interfacial regions using ab initio molecular dynamics. In-liquid ordering was determined using unsupervised learning techniques, i.e., structural fingerprinting, dimensionality reduction, and cluster analysis. Sc atoms ordered the surrounding liquid Al atoms by forming Sc-centered polyhedrons, while liquid-Al/Al3Sc interface manifested planar ordering that resembled {100}fccâˆ’Al. Both structures were geometrically persis- tent but constitutionally transient, i.e., they exchanged Al atoms with the surrounding liquid. This behavior was rationalized on the basis of their mixed metallic and covalent bond character. At a lower temperature, {100}fccâˆ’Al interfacial planes heteroepitaxially nucleated equilibrium fcc-Al, while Sc-centered polyhedrons sequentially formed metastable hcp- and bcc-Al. Using our simulations and extant experimental reports, we postulate two transformation pathways during Al-Sc solidification: (i) Scâˆ’centered polyhedrons â†’ Al3Sc â†’ liquidâˆ’Al/Al3Sc inter f acial ordering â†’ f ccâˆ’Al; and (ii) Scâˆ’centered polyhedrons â†’ hcpâˆ’Al â†’ bccâˆ’Al â†’ f ccâˆ’Al. The two in-liquid ordered structures provide an atomistic basis for the potency of Sc element, and, also, serve as possible structural metrics for designing novel Al-based alloys.

Computational Study of Non-Classical Homogeneous Crystallization in Liquid Si

Talid Sinno (University of Pennsylvania), **Abdullah Alateeqi** (University of Pennsylvania)

Keywords: Fundamentals, Modeling; Bulk; Silicon; Melt Growth; Nucleation; Energy Materials

A particularly challenging aspect of crystallization in liquid silicon is understanding the potential role of a metastable low-density-liquid (LDL) phase. The existence of a liquid-liquid transition (LLT) leading to LDL and HDL phases in liquid silicon has been of scientific interest for some time, both experimentally [1] and in simulations [2]. Although it has been suggested that the LDL phase plays an important role in lowering the crystallization barrier in both molecular liquids [3] and silicon [4], its impact has not yet been fully assessed in the latter. Moreover, the impact of impurities, such as carbon, on the role of the LDL phase in crystallization is completely unknown. The ability of empirical potentials for silicon to capture the LDL phase also is not well understood. To date, only the Stillinger-Weber (SW) potential has been used to study in detail the properties of the LDL phase in silicon liquids [5]. Here, we first investigate the formation of LDL in silicon liquids modeled by various potential model frameworks including SW, Modified Embedded Atom Method (MEAM), and Tersoff. Next, an order parameter for detecting the LDL phase is introduced and combined in a multi-order parameter scheme to calculate a nucleation free energy surface as a function of cluster sizes of both diamond crystallites and LDL clusters. This free energy surface allows us to distinguish the contribution of the LDL phase towards the overall nucleation process. A two-step nucleation process is observed whereby the crystal nucleation barrier depends strongly on the stability of an LDL precursor phase. Finally, we consider the effect of carbon impurities on the nucleation process in a silicon-carbon system. Selected potentials are employed to compute nucleation barriers in carbon contaminated silicon melts at varying degrees of carbon supersaturation and undercooling.
1. C. A. Angell, â€œFormation of glasses from liquids and biopolymers,â€□ Science 267, 1924+ (1995). 2. J. C. Palmer et al., â€œAdvances in Computational Studies of the Liquidâ€“Liquid Transition in Water and Water-Like Models,â€□ Chem. Rev. 118 (18), 9129-9151 (2018). 3. R. Kurita and H. Tanaka, â€œDrastic enhancement of crystal nucleation in a molecular liquid by its liquidâ€“liquid transition,â€□ PNAS 116 (50), 24949-24955 (2019). 4. C. Desgranges and J. Delhommelle, â€œRole of liquid polymorphism during the crystallization of silicon,â€□ JACS 133 (9), 2872-2874 (2011). 5. S. Sastry and C. A. Angell, â€œLiquidâ€“liquid phase transition in supercooled silicon,â€□ Nature Mater. 2 (11), 739-743 (2003).

Invited Talk

Selective Area Growth of N-polar GaN Nanostructures for Core-Shell Optoelectronic Devices

Matt Brubaker (National Institute of Standards and Technology), **Alexana Roshko** (National Institute of Standards and Technology), **Kris Bertness** (National Institute of Standards and Technology)

Keywords: Characterization, Devices, Growth; Low Dimensional; Nitrides; MBE; UWBG/WBG Semiconductor; Optical Materials

Core-shell nanostructures based on GaN and its related alloys enable new optoelectronic functions beyond those available from traditional planar devices, including guided and wavelength tunable optical emission for displays, large-scale periodic arrays for optical metamaterials, and non-polar devices capable of nanosecond optical response. Practical implementations require selective epitaxial growth techniques, which allow the synthesis of GaN nanowire cores (with controlled dimensions) and subsequent shell overcoating within a single growth process. In most reported accounts, these core-shell structures have been demonstrated for Ga-polar oriented nanowires and have been shown to produce strong quantum well color tuning that is related to diameter-dependent tip faceting and indium incorporation. While on-chip color tuning is advantageous for LED displays, devices such as photonic crystal lasers require specific wavelengths to excite optical resonances associated with the nanowire/array geometry and can benefit from independent control over the emission wavelength. We have developed an N-polar selective area growth process for synthesis of core-shell structures by molecular beam epitaxy that produces low color tuning relative to Ga-polar nanowires and effectively decouples the emission wavelength from the array geometry. This talk will cover the polarity control techniques used to obtain N-polar oriented nanowire cores on silicon substrates, the effect of line-of-sight shadowing on the shell layer growth/properties, and core-shell LEDs produced by N-polar selective area epitaxy.

Invited Talk

Buckets of Transistors: Scalable Nanoelectronic Devices via Bottom-up Crystal Growth and Area-Selective Processes

Michael Filler (Georgia Institute of Technology)

Keywords: Devices, Growth; Low Dimensional; Silicon; CVD, ALD; Energy Materials, Optical Materials

This talk will describe our efforts to modularize nanoelectronic devices and scale-up their manufacturing. Modularization at the device level promises an unprecedented combination of electronic performance, cost, and function; opening the door to systems that are natively heterogeneous, on-demand manufacturable, physically reconfigurable, and/or dispersible. â€˜Nanomodularâ€™ device fabrication synergistically combines multiple bottom-up and area-selective processes: (i) vapor-liquid-solid semiconductor nanowire growth, (ii) a new nanoscale polymer masking process, and (iii) atomic layer deposition. Our approach yields single-crystalline, high mobility nanowires with nanoscale coaxial thin films self-aligned to the internal dopant profile. In parallel, we are developing the Geode process to increase manufacturing throughput by several orders-of-magnitude. This scale-up is made possible by an unconventional substrate â€“ the interior surface of hollow silica microcapsule powders â€“ on which nanowire growth and subsequent processing occurs. Collaborative efforts are also enabling nanowire property characterization in a high-throughput, non-contact fashion and high-resolution interconnection of nanomodular devices to form functional circuitry.

Nanoscale selective area growth of ultra-high density InGaN/GaN QDs for visible emission patterned by diblock copolymer

Cheng Liu (University of Wisconsin Madison), **Nikhil Pokharel** (University of Wisconsin Madison), **Qinchen Lin** (University of Wisconsin Madison), **Dominic Lane** (The University of Adelaide), **Miguel A**. **Betancourt Ponce** (University of Wisconsin Madison), **Padma Gopalan** (University of Wisconsin Madison), **Nelson Tansu** (The University of Adelaide), **Chirag Gupta** (University of Wisconsin Madison), **Shubhra S**. **Pasayat** (University of Wisconsin Madison), **Luke Mawst** (University of Wisconsin Madison)

Keywords: Growth; Thin Film; Nitrides; CVD; UWBG/WBG Semiconductor; Optical Materials, Quantum Materials

Several approaches have been developed to create III-nitride quantum dots (QDs) for UV-VIS LED/laser applications due to their supreme properties, including lower threshold current densities, higher differential gain, less sensitivity to dislocation density, better carrier confinement compared to traditional quantum well (QW) emitters. QDs formed by Stranski-Kranstanov (SK) growth mode or selective area growth (SAG) on lithography patterned templates have demonstrated emission ranging from ultraviolet to visible [1-3]. However, the devices either suffer from wide full-width half maximum (FWHM) spectra or low QD density, which hinder the further development of such devices. Recently, a top-down approach using quantum-size-controlled photoelectrochemical etching (PEC) process was reported showing both high-density QD 1011cm-2 together with as narrow as 6 nm FWHM [4]. Alternatively, we developed bottoms-up controllable pathway for ultra-high density InGaN QD formation through diblock co-polymer lithography, followed by selective area MOCVD growth. However, no strong InGaN QD emission was observed, besides a wide spectral defect-related peak [5-6]. In this work, we continued optimizing the nanometer scale SAG on the diblock co-polymer patterned template and successfully achieved emission wavelengths of 483nm and 517nm from the InGaN/GaN QDs at RT. These wavelengths are longer than that from a co-loaded planar structure (456nm and 466nm), which can be attributed to the thicker InGaN layer caused by the enhanced growth rate during SAG, as well as the higher indium incorporation. The InGaN/GaN QD active region structure consists of 10nm GaN, 1.5nm InGaN and 3.5nm GaN, all of which are calibrated on a planar template. After the growth, The QD size was measured as 22 nm with a standard deviation of 2.3 nm. The QD density is counted as 7 - 9 x 1010 cm-2, which is much higher than site-controlled QDs, and comparable to SK QD and PEC QD. This study also investigated the growth mechanism by growing QDs with different thicknesses (5nm â€“ 15nm). The SEM images show that the (In)GaN grows faster near the nanopattern mask edge at the early stage, which is similar to the phenomenon observed from larger-scale SAG. As the growth continues, the regrown material exceeds the dielectric mask height, and merges towards the opening center, forming a pyramid structure. Clear facets can be observed from this growth stage. The consequent growth will be along semipolar planes, enlarging the pre-formed pyramid.

Invited Talk

Nanoparticle Assembly into Ordered Superlattices: When and Why these 'Artificial Atoms' Break Conventional Rules for Crystallization

Robert Macfarlane (MIT)

Keywords: Fundamentals; Nanoparticles; Self-Assembly, Solution Growth

Crystallization is a complex phenomenon that can occur with building blocks of a wide range of sizes, from individual atoms to macroscopic particles. Fortunately, these crystals made across different length scales can use the same structural descriptors to define both their symmetry and defect structures, providing a common language to explain and understand crystallization processes via a generalizable framework. Indeed, nano- and microparticles capable of forming ordered crystals are sometimes called "artificial atoms" in the context of programmable self-assembly, due to the structural similarities between particle superlattices and actual atomic crystals. However, while the crystal structures that can be observed at the atomic, nano, and macroscopic length scales might be structurally identical, the physical forces governing crystal stability at each of these sizes can be radically different. As a result, even if the thermodynamic end points of crystal growth look identical, the physics and chemistry governing both nucleation and growth can lead to unique intermediate structures depending on the size of the individual crystallite building blocks. In this talk, we will present recent work on a self-assembling nanoparticle construct we have dubbed the "nanocomposite tecton" (NCT), which uses supramolecular interactions to guide nanoparticles to assemble into different crystallite geometries. We will demonstrate that NCTs can crystallize with unit cell symmetries, crystal habits, phase transition, and defects that mimic those predicted based on analogies to traditional atomic crystallization. We will also elucidate the conditions under which these analogies break down, leading to non-classical nucleation and growth, complex out-of-equilibrium structures, and unexpected unit cell geometries. NCTs therefore provide an interesting tool for both expanding our knowledge of fundamental crystallization behavior and driving the formation of sophisticated hierarchical crystal structures that are either uncommon or completely unobserved in atomic crystal growth.

Gallium doped zinc oxide nanowires for quantum information applications: optical characterization of doping

David Lister (Department of Physics, Simon Fraser University), **Colton Lohn** (Simon Fraser University), **Shirin Riahi** (Simon Fraser University), **Simon Watkins** (Simon Fraser University)

Keywords: Characterization, Defects, Growth; Low Dimensional; II-VI; OMVPE; luminescence; Quantum Materials

Zinc oxide has been investigated for several decades due to its direct bandgap, and relative ease of n-type doping. Among the commonly investigated compound semiconductors, ZnO has the lowest spin-orbit coupling. This has recently been shown to result in long spin-lattice relaxation times for donor spins compared with other compound semiconductors, making ZnO a promising platform for quantum information applications.[1] Basic steps for manipulating donor spins, such as optical pumping and coherent population trapping have been demonstrated recently in single ZnO nanowires (NW) grown by organometallic vapor phase epitaxy.[2] Control of donor dopant concentration in ZnO NWs while simultaneously controlling the morphology is a challenging task. In the paper we present details of the OMVPE crystal growth and optical properties of self -assembled ZnO NW grown on sapphire substrates. We control the morphology of Ga-doped NWs by a couple of methods, including direct growth from the vapor phase, as well as a core-shell method involving growth of an undoped core followed by a lateral shell. Controlled Ga doping was achieved by use of triethylgallium. Optical control of qubits depends critically on reducing inhomogeneous linewidth broadening which depends strongly on the impurity concentration. Optical pumping is typically achieved by generating excitons localized to individual donor spins. Characterization of dopant concentrations in NWs is a challenging task. In this work we investigate the effect of dopant density on donor bound exciton photoluminescence (PL) linewidth at low temperatures. We use a simple pair model in which a single exciton can be localized at pairs of donors with varying separation modelled by a random impurity distribution. In this model, nearby pairs have a larger binding energy than distant pairs resulting in a strong redshift of PL for higher doping. Doping values obtained from the pair model were compared against the gas phase mole fraction as well as nanoprobe resistivity measurements and showed reasonable agreement. References [1] Xiayu Linpeng, Maria L.K. Viitaniemi, Aswin Vishnuradhan, Y. Kozuka, Cameron Johnson, M. Kawasaki, and Kai-Mei C. Fu, Phys. Rev. Applied 10, 064061 (2018) [2] M. L. K. Viitaniemi, Christian Zimmermann, Vasileios Niaouris, Samuel H. Dâ€™Ambrosia, XinWang, E. Senthil Kumar, Faezeh Mohammadbeigi, Simon P. Watkins, and Kai-Mei C. Fu, Nano Letters 22 2134 (2022)

Invited Talk

Development of mid- and long-wavelength infrared detectors and focal plane arrays in JPL

Alexander Soibel (Jet Propulsion Lab), **David Z. Ting** (JPL), **Arezou Khoshakhlagh** (JPL), **Cory J. Hill** (JPL), **Sir B. Rafol** (JPL), **Anita Fisher** (JPL), **Sam A. Keo** (JPL), **Sarath D. Gunapala** (JPL)

Keywords: Devices; superlattice; III-Vs (Traditional); MBE; Narrow Semiconductor; Quantum Materials

The InAs/InAsSb (gallium-free) type-II strained-layer superlattice (T2SLS) offers numerous advantages for the infrared detectors and focal plane arrays (FPAs). Innovative detector architectures such as barrier structures, in particular nBn devices, offer significant improvement in the performance GaSb-based alloys and superlattices. In this presentation I will discuss recent developments of mid- and long- wavelength infrared detectors and FPAs based on the barrier infrared detector (BIRD) architecture and their use in various remote sensing instruments.

Invited Talk

Purcell Effect versus Auger Recombination in Variable Thickness Superlattices in Resonant Cavity Mid Infrared LEDs

John Prineas (University of Iowa), **Katrina Schrock** (University of Iowa), **Matthew Bellus** (Firefly Photonics), **David Montealegre** (University of Iowa), **Logan Nichols**

Keywords: Characterization, Devices, Growth, Modeling; Low Dimensional; III-Vs (Traditional); MBE; Narrow Semiconductor, Antimonides; Optical Materials

Mid-infrared light emitting diodes (LEDs) have long been of interest as sources in optical chemical sensors of gases and biomolecules and more recently in thermal scene generation. The latest stage of advancement introduced the use of interband cascaded active regions of either superlattices (SLs) or quantum wells (QWs). Superlattices have come to dominate mid-infrared photodiode detectors compared to alloys because they are highly effective at suppressing Auger scattering, a nonradiative recombination mechanism. W-quantum wells have dominated mid-infrared laser devices, both due to superior Auger suppression and to lower threshold, and other benefits of two-dimensional confined structures. More recent efforts have focused on improving mid-infrared LED device efficiency through use of resonant cavities and half-cavities (i.e only one mirror), making use of a Purcell effectâ€”which can enhance both radiative efficiency and light extraction efficiencyâ€”by placing emission regions at the antinodes of the standing wave. Both SLs and QWs offer their own advantages to mid-IR devices. QWâ€™s and superlattices have comparable Auger coefficients, while a SL emission region can be thicker, allowing for lower Auger recombination through operating at lower carrier density. On the other hand, QWs are easier to position at the peak of field antinodes in a cavity to take maximal advantage of the Purcell effect because they are thinner. Here, we explore the trade space of Purcell enhancement versus Auger recombination effects in variable thickness W-SLs from very thick down the W-QW limit to see which is the superior approach in LEDs. We focus on room temperature infrared cavity LEDs operating at 3.3 Âµm, which coincides with an important absorption resonance in methane, and low temperature mid-infrared cavity LEDs, important for LED arrays in projectors. We find that the Purcell effect strongly enhances light extraction in both structures, with less than a factor of two penalty for thick versus thin quantum wells. On the other hand, nonradiative Auger recombination scales inversely with the square of emission region thickness (carrier density). However, the thickest W-SLs do not perform well. We find intermediate thickness W-SLs outperform W-QWs in resonant cavity LEDs at all measurable current densities. The 3.3 Âµm room temperature devices have peak WPE of about 0.4% without any backside antireflection coating or roughening, and low temperature devices with peak wallplug efficiency exceeding 1.4%.

Barrier heterostructures with bulk InAsSb absorbers for high operating temperature long-wave infrared sensors

Jingze Zhao (Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook, NY 11794), **Jinghe Liu** (Stony Brook University), **Kevin Kucharczyk** (Stony Brook University), **Dmitri Donetski** (Stony Brook University), **Gela Kipshidze** (Stony Brook University), **Gregory Belenky** (Stony Brook University), **Stefan P. Svensson** (CCDC U.S. Army Research Laboratory)

Keywords: Characterization, Growth; Bulk, supperlattice; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials

Application of barrier heterostructures with InAs/InAsSb SLS absorbers (nBn) grown on GaSb has a transformative impact on infrared sensing technology: in mid-infrared range InAsSb-based sensors replaced InSb due to significant increase of operating temperatures and approached the performance of HgCdTe diodes at T =130 K [1]. In long-wave infrared (LWIR) range design of InAs/InAsSb SLS on GaSb platform implies the growth of heavily strained InAsSb with large Sb compositions balanced with thick InAs layers leading to reduced fundamental absorption and vertical hole mobility. In order to improve the fundamental absorption and the hole mobility in LWIR nBn detectors we pursued the development of barrier heterostructures with bulk InAsSb absorbers grown by MBE on compositionally graded GaInSb metamorphic buffers on GaSb substrates. For extension of the responsivity to longer wavelengths the InAsSb absorbers were grown with Sb composition of 54 % corresponding to the minimum of the energy gap. For that the top of the buffer layer and the virtual substrate had the lateral lattice constant of 6.28 A. The heterostructures were grown with 2-um thick absorbers unintentionally doped and Te-doped to the target level of 3x1015 cm-3. The Al(Ga)InAsSb barriers lattice-matched to the absorber had a 70 % indium composition which allowed the barrier growth without an interruption for the change of the indium source temperature. The growth without the interruption helped to preserve the quality of the top layer of the absorber. In order to optimize a turn-on bias the Ga composition was varied. Temperature dependences of the minority hole lifetime were measured by time-resolved photoluminescence with the peak excess carrier concentration of a 1e16 cm-3 level. The longest hole lifetime values of 124 ns and 103 ns for undoped and doped absorbers, respectively, were observed at T = 77 K. The data imply that the hole lifetime was limited by Auger recombination. Due to superior hole mobility of 1000 cm2/Vs reported earlier the detectors with bulk InAsSb absorbers have a potential to exceed the performance to the SLS-based devices. The vertical hole mobility in LWIR short-period InAsSb-based SLS absorbers with a bulk-like absorption grown on metamorphic buffers will be discussed. The project was supported by DEVCOM Army Research Laboratory through the Center for Semiconductor Modeling and by Army Research Office award W911NF2010109. 1. A. Rogalski, P. Martyniuk, M. Kopytko, P. Madejczyk, S. Krishna, â€œInAsSb-Based Infrared Photodetectors: Thirty Years Later Onâ€□, Sensors, 20(24), 7047 (2020).

Molecular Beam Epitaxy of Binary and Ternary Manganese and Chromium Nitrides

Brelon May (Idaho National Laboratory), **Kevin Vallejo** (Idaho National Laboratory), **Krzysztof Gofryk** (Idaho National Laboratory), **Sandra Julieta Gutierrez-Ojeda** (Universidad Nacional Autonoma de Mexico), **Gregorio H. Cocoletzi** (Benemerita Universidad Autonoma de Puebla)

Keywords: Growth; Thin Film; Nitrides, Novel; MBE; Narrow Semiconductor; Energy Materials, Quantum Materials

Transition metal nitrides have exceptional properties and are used in a wide variety of electrochemical, structural, photochemical, and plasmonic applications. Among these compounds Mn- and Cr- nitrides have shown exceptional potential for magnetic sensing and spintronics. The MnxNy system is complex with several different metastable phases both predicted and experimentally realized. CrxNy has two primary phases, cubic (CrN) and hexagonal (Cr2N), which exhibit desirable mechanical, thermal, wear, anti-corrosion, thermoelectric properties. Recent studies have provided valuable insights into the growth and formation of phases of both materials using various vapor deposition techniques. However, there are conflicting reports on the electrical and magnetic properties of CrxNy which could be attributed to impurities, nitrogen vacancies, substrate effects, and strain. This controversy calls for a more detailed study and preparation of high-quality monocrystalline CrN to investigate he intrinsic physical properties. This study uses molecular beam epitaxy to synthesize epitaxial thin films of different Mn-N and Cr-N phases. The electrical and magnetic properties of these films are investigated with the rocksalt MnN and CrN both showing metallic behavior, with the latter showing a magnetic transition ~280K. However, when combining these materials at similar growth conditions, instead of maintaining the rocksalt structure, a new ternary cubic phase of MnxCryN is obtained which shows narrow-gap semiconducting behavior. This work prevents and avenue for the epitaxial integration of metallic, magnetic, and semiconductor materials

Invited Talk

Extremely low excess-noise and high gain AlxGa1-xAsSb avalanche photodiodes lattice matched to InP substrates

Seunghyun Lee (The Ohio State University), **Xiao Jin** (University of Sheffield), **Hyemin Jung** (The Ohio State University), **Harry Lewis** (University of Sheffield), **Yifan Liu** (University of Sheffield), **Bingtian Guo** (University of Virginia), **Christoph Grein** (University of Illinois at Chicago), **Theodore**. **J**. **Ronningen** (The Ohio State University), **John**. **P**. **R**. **David** (University of Sheffield), **Joe**. **C**. **Campbell** (University of Virginia), **Sanjay Krishna** (The Ohio State University)

Keywords: Characterization, Devices, Growth; Thin Film; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials, Quantum Materials

The ability to detect low numbers of photons in the 1400-1550 nm wavelength range is crucial for remote sensing and long-range LiDAR applications. Linear mode avalanche photodiodes (LmAPDs) with internal gain (M) provide high detection sensitivity, making them a popular choice over PIN diodes. However, this gain comes at the cost of excess noise (F) due to the stochastic nature of the impact ionization process. The best commercially-available LmAPDs for 1550 nm use InGaAs absorbers and InP or InAlAs multipliers with a separate absorption, charge, and multiplication (SACM) architecture. These devices have a relatively low gain (~30) and high excess noise factor (> 10), limiting their performance. Recently, we have shown a breakthrough in the development of a high-performance avalanche photodiode (APD) that operates at room temperature and achieves high gain and reduced excess noise. The APD is based on a GaAsSb/AlGaAsSb SACM architecture. The key to its success is the use of high-quality AlxGa1-xAsSb (where x ranges from 0 to 1) grown by solid-state molecular beam epitaxy (MBE) with a low background doping concentration (< 5 X 1015 cm-3). Optimization allows for precise control over the growth of the material, resulting in high-quality crystals with low impurity concentrations. The resulting APD has a high gain, with a multiplication factor (M) of around 278, and reduced excess noise, with an excess noise factor below 3. This presentation will discuss the technical challenges involved in designing and growing the materials for the APDs, as well as exploring novel approaches to further improving their performance. Overall, the development of high-performance LmAPDs with reduced excess noise and high gain at room temperature presents an exciting opportunity for remote sensing and long-range LiDAR applications. With further improvements in material growth and design optimization, these devices may lead to significant advances in the field.

Invited Talk

Development of SiGeSn Technology for Monolithic Infrared Silicon Photonics

Wei Du (University of Arkansas), **Shui-Qing Yu** (University of Arkansas)

Keywords: Characterization, Devices, Growth; Bulk, Thin Film; Novel, all group IV; CVD; Narrow Semiconductor; Optical Materials

Recent studies of SiGeSn semiconductors have opened a new route for the development of all-group-IV-based optoelectronic devices. The unique optical properties of SiGeSn alloys include: i) a true direct bandgap material in favor of band-to-band transition LEDs and lasers; ii) SiGeSn-based devices can be monolithically integrated on Si substrates; iii) the lattice constant and bandgap energy can be controlled independently which enables a variety of heterostructures; iv) the operational wavelengths of emitters and photodetectors cover the broad short-wave, mid-wave, and long-wave infrared range; and v) the full complementary metalâ€“oxideâ€“semiconductor (CMOS) compatibility allows for low-cost and high-yield foundry manufacturing. This talk will present the recent progress for the development of SiGeSn technology, including the material growth using commercial chemical vapor deposition (CVD) reactor, demonstration of optically pumped and electrically injected lasers, light emitting diodes (LEDs) and IR photodetectors. The SiGeSn materials were grown on Ge buffered Si substrates using a commercial CVD reactor and low-cost precursors. After growth, the Si and Sn compositions were determined by Secondary Ion Mass Spectrometry (SIMS); the strain was extracted by reciprocal space mapping (RSM) of X-ray diffraction (XRD) measurement; the layer thickness and material quality were confirmed by transmission electron microscopy (TEM) image. The ridge-waveguide-based edge-emitting lasers and photodetectors were fabricated by using standard lithography and wet etching processes. For the optically pumped lasers, the maximum lasing temperature reaches 270 K. For the electrically injected lasers, the threshold current densities were measured as 0.74 and 3.9 kA/cm2 at 10 and 100 K, respectively. At 10 K, the maximum peak power was measured as 2.7 mW/facet. The significantly reduced peak linewidth at above threshold confirms the onset of lasing. For the photoconductors, D* was measured and compared with commercial photodetectors. At 2.4 Âµm, the peak D* of 1.1Ã—1010 cmâˆ™Hz1/2W-1 was achieved with 12.5% Sn device. The longest cutoff at 3.65 Âµm was obtained. The IR photodiodes was systemically studied. The passivated device overperforms the non-passivated one and shows a little better D* compared to the PbSe detector from 1.5 to 2.2 Âµm.

Invited Talk

InAs/InAsSb type-II superlattice and its applications in devices

Yong-Hang Zhang (Arizona State University)

Keywords: Devices, Growth; Thin Film; III-Vs (Traditional), sensor and imaging; MBE; Narrow Semiconductor; Quantum Materials

The study of InAs/InAsSb T2SL on GaSb and its application to IR lasers was started in the early 90â€™s. The observation of a 412 ns long carrier lifetime in a long-wavelength infrared (LWIR) InAs/InAsSb T2SL in 2011 triggered extensive research on the fundamental materials properties and device applications. Pressure-dependent photoluminescence experiments revealed some underlying material physics of these long carrier lifetimes. Some of the device applications will also be discussed.

Long-wave infrared beam steering with InAsSb-based plasmonic phased arrays

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Keywords: Devices, Modeling; Bulk; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials

The infrared beam steering with optical phased arrays (OPA) is a promising technology for LIDAR and communications. In mid-wave infrared range the OPAs for azimuthal beam steering based on electro-optical effect in $LiNbO_3$ and various approaches to refractive index modulation in III-V compound heterostructures have been reported [1-2]. In this work, we demonstrate the possibility of the beam steering in long-wave infrared (LWIR) range with an array of InAsSb-based waveguides. The large absorption coefficient allows the effective modulation of carrier-induced change of refractive index reaching 0.05 at 77 K for $InAsSb_{0.4}$ with electrical carrier injection [4]. The devices were designed to operate at a 10.6 um with the laser beam coupling to the phase modulation section with gratings. Due to high index modulation large beam steering angles can be realized with relatively short phase changing sections. The considered nBp heterostructures consisted of 2-um thick InAsSb absorbers on AlInSb and GaInSb graded buffers grown on GaSb. The top metal contact served for the injection of excess carriers and for the plasmonic-assisted optical mode confinement. Various heterostructure designs with variations of the Al(Ga)InAsSb barrier thickness, waveguide widths, etching depths, waveguide spacing and metallization layouts were considered. The designs were aimed at the 30° azimuthal steering angle. For designs with AlInSb buffers optimizations showed a 28 cm^{-1} optical losses with a 60 % mode confinement with the absorber. The designs with GaInSb buffers showed the optical losses of 17 cm^{-1} at the mode confinement of 44 %. The project was supported by DEVCOM Army Research Laboratory through the Center for Semiconductor Modeling and by Army Research Office award W911NF2010109. [1]. Y. Xu, K. Zheng, J. Shang, W. Yuan, S. Fu, H. Lu, Y. Wang, and Y. Qin, Opt. Lett. 47, 329-332 (2022) [2]. L. Flannigan, L .Yoell, C. Xu, J. Opt. 24 043002 (2022) [3]. D. Donetsky, J. Liu, G. Kipshidze, L. Shterengas, G. Belenky, W. L. Sarney, and S. P. Svensson, Appl. Phys. Lett., 115, 081102 (2019). [4]. J. Liu, D. Donetsky, H. Jiang, G. Kipshidze, L. Shterengas, G. Belenky, W. L. Sarney, and S. P. Svensson, J. Appl. Phys., 128, 083101 (2020).

Crack suppression of high Al-mole-fraction AlGaN layers on patterned GaN substrates for ultraviolet laser diodes

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Keywords: Devices, Growth; Thin Film; Nitrides; CVD, VPE; UWBG/WBG Semiconductor; Optical Materials

Tensile strain limits the growth of adequately thick and/or high Al-mole-fraction AlGaN epitaxial layers on GaN substrates, and the growth of layers having thickness beyond the critical layer thickness results in cracking of the film. We have described a novel approach employing non-planar growth (NPG) that enables the deposition of crack-free AlGaN layers with relatively thick and high Al-mole-fraction on GaN substrates patterned into rectangular mesas with adequately large area for the fabrication of UV LDs.[1, 2] In this work, we demonstrate a UV-A LD fabricated with the NPG approach. A UV-A multiple-quantum-well LD structure was designed and grown by MOCVD on the NPG patterned (0001) GaN substrate. Stripe-shaped NPG mesas were formed on the substrate by conventional dry etching. The direction of the stripe mesas was aligned to be parallel to the m-axis of GaN. The widths of the NPG mesas were set to be ~100 Âµm. The CL in upper and lower side of the active layers are composed of doped AlGaN SPSLs with average Al mole fraction and combined thickness of 0.16 and 1100 nm, respectively. The NPG LDs have no cracks on the top surface of several-mm-long NPG mesas while the planar sample without mesa formation has a dense crack-network on the grown surface. The suppression of the crack formation is confirmed to be attributed to an anisotropic relaxation of the strain in the AlGaN SPSL which was enabled by the elastic deformation of GaN layer along the direction perpendicular to the stripe mesa. Fabry-Perot LD devices with cleaved facet mirrors were fabricated on the NPG mesas. The device with a dimension of 12 Âµm ridge and 750 Âµm cavity length shows stimulated light emission at a wavelength of 371.4 nm with pulsed current injection (100 ns pulses at 1kHz) at 300K. The devices were probe tested without heatsinking and only a back-side reflective facet coating. A relatively high threshold current density of 12.2 kA/cm2 is attributed to the absence of a front side mirror coating. This first successful demonstration of UV-A LDs on the NPG platform clearly indicates that this approach enables us to achieve high performance UV-A LDs with thick and high composition AlGaN layers beyond critical layer thickness by relaxing the tensile stress in the AlGaN layers. References [1] F. Mehnke et al., J. Appl. Phys. 131, 073103 (2022). [2] Y. Ando et al., J. Cryst. Growth 607, 127100 (2023).

Nitrogen-Implanted Floating Guard Rings as Edge Termination for kV-Class Vertical GaN PIN Rectifiers for Breakdown Voltage Improvement and Premature Breakdown Study by Sub-bandgap Photoluminescence

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Keywords: Characterization, Defects, Devices, Growth; Bulk; III-Vs (Traditional), Nitrides; CVD, Ion Implantation; UWBG/WBG Semiconductor; Energy Materials

As a wide-bandgap material (~3.4eV) gallium nitride (GaN) is a promising material for high-power electronics. GaN can sustain high breakdown voltage and high-temperature operation, providing higher switching frequencies with lower power losses. Edge termination technology is of critical importance in improving breakdown voltage of GaN p-n diodes. Vertical PIN rectifiers offer avalanche breakdown capability as well as a vertical depletion mode which can mitigate surface breakdown issues when compared to lateral structures. Our prior work has shown that multiple 1-2 Âµm wide floating guard rings (FGRs) formed by nitrogen implantation effectively improve the breakdown voltage (BV), achieving uniform BV >1.2kV with a low turn-on voltage of 3.5V. The MOCVD-growth device structure of this study consisted of a 0.5Î¼m n-GaN:Si ([n]=6Ã—1018 cm-3), 8.5Î¼m GaN:uid drift layer, a 450nm p-GaN:Mg ([p]=1Ã—1018cm-3), and a 20nm p+-GaN:Mg ([Mg]=1Ã—1020cm-3) on an ammonothermally grown bulk (0001) GaN substrate. The J-V characteristics at 300K of two batches of devices on separate GaN wafers sample I and II, were each measured for 400 devices consisting of device diameters of 100Î¼m and 200Î¼m. Sample I had an overall average BV of 1209Â±229V at 0.01A/cm2, with 274 out of 400 (68.5%) measured devices reaching BV>1.2kV. Sample II had an overall average BV of 1095VÂ±210V at 0.01A/cm2, with 241 out of 400 (60.25%) measured devices able to reach BV>1.2kV. To evaluate the impact of material quality on lower-BV devices, photoluminescence (PL) imaging with an excitation wavelength of 405nm was performed before growth, after growth, and prior to device processing. There is no significant sub-bandgap PL observed for the GaN substrates before epitaxial growth. After epitaxial growth, the panchromatic PL intensity as well as PL image and BV correlation shows that lower measured BV is related to the lower PL intensity features. Wafer-scale imaging indicates that lower PL intensities are related to higher Mg doping concentrations, as the PL emission of donor-acceptor pair recombination is suppressed in heavily doped GaN:Mg layers. It is found that the PL intensity can be correlated to macro-defects in the GaN epi layers. Cracks, triangular hillocks, particles, and surface roughness induced by step bunching contribute to the PL signal as well as increased leakage current density and lower BV of the devices. Acknowledgement This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Lattice matched virtual substrates for Al-X-N epitaxy

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Keywords: Characterization, Growth; Thin Film; Carbides, Nitrides; MBE, Sputtering; UWBG/WBG Semiconductor; Energy Materials, Scintillator Materials

Ternary aluminum-containing nitrides (AlyX1-yN) demonstrate properties suitable for a wide variety of next-generation opto- and power electronic applications.[1,2] These alloys often lack suitable lattice-matched substrates, ultimately limiting either crystal quality or the accessible composition range before defects or decomposition begin to occur. We have identified the (111) plane of transition metal carbides and nitrides as lattice matched â€œvirtualâ€ substrate layers that have the additional benefits of electrical conductivity, necessary for vertical devices, and appropriate coefficients of thermal expansion for the growing and grown nitride layer.[3] Here we investigate RF sputter growth and optimization of epitaxial (111)-oriented TaC and ZrN for AlyGa1-yN and AlyGd1-yN, respectively. We confirm phase purity and epitaxial orientation and optimize for full-width half max (FWHM) of in- and out-of-plane film components to limit strain and resulting defects. We grow these proof-of-concept films on sapphire substrates with the understanding that either conductive substrates, epitaxial liftoff, or standalone substrates must be used for a truly vertical device. In the case of TaC, films are grown directly on sapphire substrates at temperatures above 800 C. X-ray diffraction (XRD) and transmission electron micrographs (TEM) demonstrate epitaxial registry of the grown layer to the substrate. We investigate the effects of high temperature face-to-face anneals in an argon environment and observe significant improvements to the FWHM of in-plane (111) and out of plane (113) peaks. Atomic force microscopy (AFM) reveals changes in morphology from the columnar grains typical of sputtering to a step-terrace surface suitable for epitaxial growth of AlyGa1-yN compositions near y=0.5. We successfully nucleate AlyGa1-yN thin films using molecular beam epitaxy on both TaC and AlN and the defect and crystal structure are analyzed. We also grow (111)-oriented ZrN buffer layers as virtual substrates for the emerging AlyGd1-yN, which shows initial promise in optoelectronics and neutron detection. Here, an epitaxial TiN layer is deposited on sapphire and then a Ti-Zr-N grade is employed to seed growth of (111)-oriented ZrN, lattice matched to Al0.8Gd0.2N. Structure, morphology, and strain are analyzed using XRD and AFM. Initial Al0.8Gd0.2N thin film growth is initiated both in-situ and ex-situ and measure film quality and orientation due to other substrates such as silicon. Next steps to further reduce defect density and improve substrate quality are considered. [1] R. J. Kaplar et. al, ECS J Solid State Sci Tech 6 (2) 2017 [2] R. W. Smaha et. al, Chem Mater, 34 (23) 2022 [3] D. M. Roberts et. al, arXiv:2208.11769 2022

Computational Fluid Dynamics Modeling of a Novel High-Pressure Spatial Chemical Vapor Deposition Reactor (HPS-CVD) Design for Growth of Indium-Containing Nitrides

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Keywords: Growth, Technology/Equipment; Thin Film; Nitrides; CVD; Narrow Semiconductor, UWBG/WBG Semiconductor; Energy Materials, Optical Materials

Epitaxial growth of high-indium-content nitrides, such as In(1-x)Ga(x)N or Al(x)In(1-x)N, is challenging due to the relatively low dissociation temperature of InN into indium metal and nitrogen gas necessitating growth temperatures which are sub-optimal for growth of device-quality films. Increasing the gas pressure (up to 15 atm) within a horizontal flow metal-organic chemical vapor deposition (MOCVD) tool has been shown to be effective at increasing the growth temperature of InN and at increasing the indium incorporation at a certain growth temperature. Unfortunately, higher pressures and resultingly higher fluid densities result in fluid dynamic and heat transfer challenges which result in turbulence and loss of group-III source material prior to incorporation on the substrate. To address the fluid dynamic challenges associated with high-pressure MOCVD growth of (nitride) materials, a new MOCVD reactor has been proposed which carries the potential to operate at super-atmospheric pressures (up to 100 atm). Key to this innovative design is the spatial separation of precursors prior to mixing in the boundary layer immediately above the substrate. This contribution will discuss the current state of development of this tool via a discussion of computational fluid dynamic simulations performed using the computational fluid dynamics software, COMSOL Multiphysics. Fully coupled flow and thermal studies of this novel high-pressure spatial chemical vapor deposition (HPS-CVD) tool will be presented and suitable operating windows for super-atmospheric conditions discussed to highlight the viability of this platform.

XRD analysis of relaxation of non-biaxial strain at the semipolar interface in AlGaN grown via heteroepitaxial FACELO

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Keywords: Characterization, Growth; Thin Film; Nitrides; CVD, VPE; UWBG/WBG Semiconductor; Energy Materials, Optical Materials, Quantum Materials

The realization of strain-free AlGaN films with low dislocation density is an essential building block for the development of next-generation ultraviolet optoelectronics and power electronics. As native AlGaN substrates do not exist, there is a growing interest in enabling AlGaN growth on single-crystal GaN substrates. However, conventional planar epitaxy of AlGaN on c-plane GaN results in cracking in the first tens of nm due to the lattice mismatch-induced tensile stress of several GPa. In this study, we demonstrate the efficacy of the heteroepitaxial facet-controlled epitaxial lateral overgrowth (FACELO) approach for the growth of relaxed AlGaN on single-crystal GaN substrates. An x-ray diffraction (XRD) analysis model is developed for studying the strain state and composition of AlGaN epilayers grown using this method. By patterning the native c-plane substrate via FACELO, a semipolar heterointerface is achieved for strain relaxation followed by returning to a c-plane surface for subsequent device layer growth. AlGaN growth on semipolar GaN facets results in a finite resolved shear stress, thereby activating the wurtzite primary slip system. This allows for strain relaxation via misfit dislocations at the heterointerface. For the study, 5 Âµm-thick Al0.15Ga0.85N layers were grown on FACELO GaN via metalorganic chemical vapor deposition. No cracks were observed, indicating that alternate relaxation mechanisms were active early during AlGaN growth. The semipolar interface and the resulting strain state in FACELO require additional considerations during the XRD analysis. The structure differs from normal growth on c-plane substrates because it does not have a biaxial strain state. The structure also differs from growth on semipolar substrates because the pyramidal structures in FACELO introduce two semipolar interfaces instead of just one. As a result, the epilayer reciprocal lattice point is split by tilt contributions from each interface. Additionally, a different set of reflections is accessible compared to semipolar growth. In this study, we present a model to determine the AlGaN composition based on the non-biaxial strain state, and a prediction of the final strain state is made based on the reduction in resolved shear stress. Sources of tilt are predicted and accounted for in the calculations. It is shown that three reciprocal space maps are required to fully measure the lattice parameters and determine the composition and strain state. The strain state of the FACELO-grown AlGaN agreed with calculations based on the reduction in shear strain via misfit dislocations. The analysis is, therefore, effective for the evaluation of the relaxation scheme.

Quasi Vertical Schottky Barrier Diodes on Bulk AlN Substrates

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Keywords: Devices; Thin Film; III-Vs (Traditional), Nitrides; CVD; UWBG/WBG Semiconductor; Power devices

Aluminum Nitride (AlN) is an attractive material for extreme environment capable kV-class power devices due to its ultra-wide bandgap, high thermal conductivity, and high temperature stability. Despite these exceptional properties, there have been very few reports on devices fabricated on AlN. This is primarily due to the large activation energy of the dopants and the low formation energies of compensating point defects, which make doping a significant challenge that needs to be overcome for practical devices to be realized. Schottky barrier diodes (SBDs) on AlN have been previously reported in the literature, however, these reports show ideality factors (n) larger than 5, indicating that the current transport mechanism differs significantly from thermionic emission. This is because typical devices are fabricated on foreign substrates which provide many parallel current leakage paths. Additionally, some reports rely on unintentional doping of the AlN layers for n-type conductivity. In this work, we use point defect controlled, epi-doped layers grown on bulk AlN substrates to show near ideal Schottky diode operation in AlN. Using metalorganic chemical vapor deposition (MOCVD), a structure of 2 Âµm thick n+ Al0.8Ga0.2N ([Si] ~ 1x1019 cm-3) followed by of 1 Î¼m thick n AlN ([Si] ~1x1018 cm-3, n = 2x1015 cm-3, Âµ = 160 cm2/Vs) was grown on a c-oriented bulk AlN wafer. Device mesas were defined and etched using photolithography and Reactive Ion Etching (RIE). Subsequently, ohmic contacts were formed by depositing a large area Cr/Ti/Al/Ti/Au metal stack on the etched surface, followed by the Schottky contacts which consisted of circular Ni metal. The electrical behavior of the Schottky diodes is analyzed using I-V measurements. In the forward bias, a threshold voltage of 2 V and ideality factor of 1.17 is observed. This ideality factor is the lowest reported in the literature for diodes on AlN and indicates close to ideal device operation. Record-high currents for devices in AlN are reported with around 600 A/cm2 at 45 V. A low ON-resistance is observed of around 100 mÎ©-cm2 at 20 V forward bias. A rectification ratio (ION/IOFF) of around 1010 at Â±20 V is observed. In the reverse bias, a state-of-the art breakdown voltage of 770 V is observed. These results demonstrate the potential of AlN as a platform for extreme environment capable kV-class devices.

Ga(As,P) OMVPE on Si substrates employing surfactant Sb and Ge ion implantation

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Keywords: Growth; Thin Film; III-Vs (Traditional), Silicon; CVD, VPE; Optical Materials

The growth of III-V compound semiconductors on silicon remains an active research area with prospective high-impact applications including on-chip optoelectronics/microelectronics integration for data communication, photovoltaics, sensing and quantum photonics. Of the III-V semiconductors, GaP benefits from minimal lattice mismatch with Si and a wide range of potential device applications including lasersâ€” spanning from visible range to mid-infraredâ€”and high voltage/temperature power electronics. Despite the large 4% lattice mismatch, GaAs integration on Si has received the most attention. In general, III-V epitaxy on Si still faces many challenges including anti-phase domains, twinning, lattice and thermal mismatch and the requirement of thick buffer layers. Exploration has been mostly limited to offcut (100) substrates, with few studies on other orientations. In this work, we investigate Ga(As,P) OMVPE on Si substrates of (100), offcut (100) and (111) orientations, and the impact of an Sb surfactant on the growth. GaP nucleation, surface morphology and crystallographic twinning are studied by atomic force microscopy and 3-dimensional x-ray diffraction. The growths were carried out with triethylgallium, trimethylantimony, and phosphine as precursors, at substrate temperatures 670â€“720 C after a buffered HF etch and arsine cleaning at 780 C. Preliminary results show significant changes in nucleation morphology when exposed to Sb, with smoother surface features and increased coalescence. In addition, Ge ion implantation and selective oxidation of Si wafers is investigated for alleviating the large GaAsâ€“Si mismatch without the need for thick buffer layers. This process results in a fully strain relaxed thin Ge surface layer, which is ideal for subsequent lattice-matched GaAs OMVPE and related optoelectronic device growth. Substrate preparation and characterization of OMVPE grown GaAs will be presented. This work presents promising pathways for overcoming key challenges affecting III-V integration on Si.

Optical and Structural Characteristics of ~1.65um-emitting Quantum Dots Grown by Selective Area Epitaxy

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Keywords: Characterization, Growth; Low Dimensional, Thin Film; III-Vs (Traditional); CVD, OMVPE; Quantum confined semiconductor; Optical Materials, Quantum Materials

Semiconductor laser diodes employing quantum dot (QD) active regions are predicted to have high gain, low threshold current density (Jth) [1], and negligible temperature dependence [2] which are important for achieving high CW output power and power conversion efficiency, Î·p. Conventional Stranski-Krastanov (SK) growth method, in which compressive strain in the layer is the driving force for the nucleation of the dots, is one of the most widely used growth techniques to fabricate laser diodes in the region of wavelength of 1.5 Î¼m (C-band), both by MBE [3] and OMVPE [4]â€“[6]. Although, there has been some progress to achieve high gain and temperature insensitivity in laser devices fabricated by SK method [7], [8], this still remains a major challenge due to inherent wetting layer formation during growth process [9]. Alternately, we attempt to fabricate (InGaAs/AlInAs) quantum dots using di-block co-polymer lithography and selective area epitaxy (SAE) via OMVPE on InP substrates. This fabrication method avoids the formation of a wetting layer and decouples the QD formation from the strain state of the material. Therefore, ideally it should allow us to realize a device with temperature insensitivity and higher modal gain. Using SAE, we have previously demonstrated wavelength~1.67 Î¼m-emitting QD lasers on InP substrates with low Jth (<1.6 kA/cm2) [10], although a detailed structural analysis of the QD materials was not performed. However, the nano-patterning and SAE method also suffers with process induced non radiative recombination sites within active region, and the challenge of effective carrier injection into QDs still remain at large [11]. Additionally, the non-uniform size (height) distribution of QDs from fabrication steps leads to broadening of the PL linewidth. In this work, we focus to improve the QD uniformity by controlling different process steps like nano-pattern transfer time, CBr4 in-situ etching time and flow rate, as well as the OMVPE SAE growth conditions. High resolution z-contrast (scanning) TEM imaging reveals the structural features of the QDs with different strained barrier material (InGaAs or AlInAs). Our study reveals that non-uniform in-situ etching of InP sacrificial layer and a higher growth rate of the AlInAs barriers inside nano-holes form hillocks, which may contribute to poor optical properties. Moreover, tuning other growth conditions like growth rate, V/III ratio, temperature as well as varying quantum well size within the QDs is expected to lead to improved uniformity in the QD size distribution. References: [1] M. Asada, Y. Miyamoto, and Y. Suematsu, â€˜Gain and the Threshold of Three-Dimensional Quantum-Box Lasersâ€™, IEEE J Quantum Electron, vol. 22, no. 9, pp. 1915â€“1921, 1986, doi: 10.1109/JQE.1986.1073149. [2] Y. Arakawa and H. Sakaki, â€˜Multidimensional quantum well laser and temperature dependence of its threshold currentâ€™, Appl Phys Lett, vol. 40, no. 11, pp. 939â€“941, 1982, doi: 10.1063/1.92959. [3] S. Banyoudeh et al., â€˜Temperature-Insensitive High-Speed Directly Modulated 1.55- Î¼m Quantum Dot Lasersâ€™, IEEE Photonics Technology Letters, vol. 28, no. 21, pp. 2451â€“2454, 2016, doi: 10.1109/LPT.2016.2600508. [4] D. Gready et al., â€˜High speed 1.55 inas/ingaalas/inp quantum dot lasersâ€™, IEEE Photonics Technology Letters, vol. 26, no. 1, pp. 11â€“13, Jan. 2014, doi: 10.1109/LPT.2013.2287502. [5] D. Franke et al., â€˜Improved optical confinement in 1.55 Î¼m InAs/GaInAsP quantum dot lasers grown by MOVPEâ€™, in 2008 20th International Conference on Indium Phosphide and Related Materials, 2008, pp. 1â€“4, doi:

In-situ Reflectometry for Controlling Synthesis of 2D Materials and Heterostructures during MOCVD

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Keywords: Growth, Technology/Equipment; 2D; 2D materials; VPE; TMDC, hBN; Optical Materials, Quantum Materials

Owing to their unique properties, two-dimensional (2D) van der Waals (vdW) materials are considered promising for future optical and electronic devices. One of the key challenges for the commercial realization of 2D materials (opto)electronic devices is the controlled wafer scale synthesis of 2D materials at conditions that are compatible with established processes (e.g., CMOS). To date, metal-organic chemical vapor deposition (MOCVD) technique provides the most viable route for the synthesis of 2D materials on an industrial scale. Given the large parameter space of MOCVD and the variety of different 2D materials, in-situ metrology techniques are sought for monitoring and controlling the growth process of 2D materials on a wafer scale, but reliable techniques are still missing. Here, we implement in-situ reflectometry to monitor nucleation and growth of 2D material domains in real time on up to 200 mm silicon/SiO2 and sapphire substrates. We demonstrate that the in-situ measured reflectance intensity of transition-metal dichalcogenides (TMDs) correlates with the ex-situ measured layer coverage measured by atomic force microscopy (AFM) or scanning electron microscopy (SEM). Based on these metrology capabilities integrated with an AIXTRON close-coupled showerhead (CCS) system, we were able to synthesize 2D layers of transition-metal dichalcogenides (TMDs), graphene, hexagonal boron nitride (hBN) and their heterostructures with wafer-scale uniformity and excellent crystal quality. In particular, in-situ reflectance measurement during growth enabled the synthesis of hBN/graphene heterostructures of defined thicknesses. Overall, MOCVD coupled to in situ reflectance spectroscopy provides a promising route towards the scalable integration of high quality 2D materials for future (opto)electronic devices.

Atomically-resolved structure and composition at III-V device heterointerfaces grown by MOVPE

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Keywords: Characterization, Devices, Growth; Low Dimensional; III-Vs (Traditional); VPE

Various III/V-semiconductor based devices, like LASERs with W-type band alignment or quantum cascade lasers use spatially indirect electronic transitions to achieve their functionality. For these structures, which often contain only nanometer-thick regions of a certain composition, which are repeated throughout the device structure, the roughness and compositional (in)homogeneity across internal interfaces is often decisive for the devicesÂ´ performance. Hence probes, which enable atomic resolution across interfaces are needed to characterize these device structures and to optimize their growth conditions. We investigate Ga(As,Sb,N)/(Ga,In)(N,As)/ Ga(As,Sb,N) W-type LASER structures as well as (Ga,In)As/(Al,In)As/InP quantum cascade LASER structures, both grown by metal organic vapour phase epitaxy (MOVPE) under various conditions. The structures allow for mid-to far-infrared wavelength emission. Scanning transmission electron microscopy (STEM), applying aberration-correction, is used to investigate the materials at an atomic level with a special focus on the internal interfaces as well as on the homogeneity of the active regionÂ´s repetitions in a device stack. Combining STEM with a fast, pixelated detector allows for the acquisition of a full diffraction pattern at each scan point. From this, four-dimensional STEM (4D-STEM) datasets are available, which can be used to generate different valuable data, yielding insight not only in the composition of light elements (like N), but also on electric fields in device structures. We show that, when compared to image simulations, the information on the sample structure, composition and fields is quantitative. We will present a detailed atomic-resolution study on the composition and interface roughness and correlate our results to the device performance of the respective structures.

~ 8.1 Î¼m InP-based quantum cascade lasers grown on Si via OMVPE

Shining Xu (Uniersity of Wisconsin-Madison), **Shuqi Zhang** (Uniersity of Wisconsin-Madison), **Huilong Gao** (Uniersity of Wisconsin-Madison), **Jeremy Kirch** (Uniersity of Wisconsin-Madison), **Yiteng Wang** (University of Illinois Urbana-Champaign), **Minjoo Lee** (University of Illinois Urbana-Champaign), **Rao Tatavarti** (Microlink Devices Inc), **Dan Botez** (University of Illinois Urbana-Champaign), **Luke Mawst** (University of Illinois Urbana-Champaign)

Keywords: Devices, Growth; Thin Film; III-Vs (Traditional), Silicon; VPE; Narrow Semiconductor; Quantum Materials

Recently, by employing a direct heteroepitaxial growth monolithic integration method, some research groups have demonstrated room temperature operation from all-binary InAs-based QCLs on Si grown by MBE for long wavelength emission, at ~8 Âµm [1] and ~11 Âµm [2], and extended work to ~14 Âµm for QCL on Ge [3], showing low threshold current and pulsed device performance comparable with those on their native InAs substrate. Ternary InGaAs/AlInAs/InP-based QCLs on Si, also grown by MBE, have been reported with operating temperatures ranging from 170 K [4] to 358 K [5] for 4-5 ï□m emission wavelengths. Output powers exceeding 4 W from two facets under RT operation were recently reported[6], although threshold current densities are higher compared to the same devices on native InP substrates. Here we report what we believe to be the first OMVPE-grown ~ 8.1 Î¼m InGaAs/AlInAs/InP-based QCLs on an InP-on-Si(substrate) template employing a 35-stage lattice-matched active region, and demonstrate laser performance on the Si substrate which is comparable to that on the InP native substrate. The growth of a GaAs buffer layer was first performed on a commercially bought (001) GaP/Si substrate from NAsPIII-V GmbH via MBE. Next, an InP metamorphic buffer layer (MBL) and then full QCL structure were grown on this GaAs/GaP/Si template by OMVPE following the procedure described previously[7]. The surface morphology of the as-grown GaAs/GaP/Si template before and after the InP MBL growth, was assessed via AFM over a 100 um2 area. No antiphase domains (APD) were found on the GaAs/GaP/Si template and the RMS roughness is ~ 1.62 nm. The surface roughness was reduced to RMS~ 1.53 nm after growing the InP MBL. Electron channeling contrast imaging (ECCI) of the above samples was used to estimate the threading dislocation density (TDD). The average TDD for the GaAs/GaP/Si template was found to be ~1 x 109 cm-2, and a lower defect density of ~7.9 x 108 cm-2 after InP MBL growth. The threshold current density of QCLs on Si, ~25 Âµm-wide (3mm long) deep-etched ridge-guide devices with uncoated facets, is slightly lower than its counterpart on native InP substrate, 1.50 vs. 1.92 kA/cm2, with maximum output powers of 1.64 vs. 1.47 Watts/facet. FTIR spectrum measurements indicate the emission wavelengths of devices on Si is slightly longer than for devices on InP, 8.1 vs. 8.0 Âµm. These data further demonstrate the resilence of QCLs to a relatively high residual TDD.

Impact of tellurium doping on minority carrier lifetime in heterostructures with bulk In(Ga)AsSb absorbers

Jingze Zhao (Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook, NY 11794), **Jinghe Liu** (Stony Brook University), **Gela Kipshidze** (Stony Brook University), **Dmitri Donetski** (Stony Brook University), **Leon Shterengas** (Stony Brook University), **Gregory Belenky** (Stony Brook University)

Keywords: Characterization, Growth; Bulk; III-Vs (Traditional); MBE; Narrow Semiconductor; Optical Materials

Temperature dependences of minority carrier lifetime were measured in bulk InAsSb and Ga0.2In0.8As0.73Sb0.27 epitaxial layers grown lattice matched to GaSb for photodetector applications. Over years, measurements of carrier lifetime in bulk InAsSb lattice matched to GaSb was addressed many times for various sample growth and measurement conditions [1-3]. In this work, The heterostructures were grown by MBE at the temperatures of 430 and 450 C. The set of samples included InAsSb0.09 with unintentional doping and samples doped with tellurium. The heterostructure with the Ga0.2In0.8As0.73Sb0.27 composition. All heterostructures had the absorber thickness of 2 um. For carrier confinement bulk In(Ga)AsSb absorbers were grown on n- doped buffers and capped with 200 nm thick GaSb layers doped n-type to the level of 2x1017 cm-3. The carrier lifetime was determined by time-resolved photoluminescence measurements in the temperature range from 77 to 300 K. The peak excess carrier concentration was varied in the range from 2.5x1015 to 2 x1016 cm-3. At T = 77 K low injection minority hole lifetime values in InAsSb layers grown at 430 and 450 C were found to be 4 and 7 us, respectively. The carrier lifetime was found to be radiative-limited and increasing with decrease of excess carrier concentration. Doping with tellurium to the nominal levels of 5x1015 cm-3 and 2x1016 cm-3 resulted in significant reduction of the lifetime down to 20 and 12 ns, respectively, while the PL decay was exponential in the entire range of excitation. The heterostructure with unintentionally doped Ga0.2In0.8As0.73Sb0.27 absorber had the minority carrier lifetime of 350 ns. The lifetime temperature dependences were used for separation of the radiative and non-radiative recombination terms. This work was supported by US Department of Energy, Office of Science, award DE-SC0023165. [1] J. R. Lindle, J. R. Meyer, C. A. Hoffman, F. J. Bartoli, G. W. Turner and H. K. Choi, Appl. Phys. Lett. 67, 3153 (1995). [2] B. V. Olson, E. A. Shaner, J. K. Kim, J. F. Klem, S. D. Hawkins, L. M. Murray, J. P. Prineas, M. E. FlattÃ© and T. F. Boggess, Appl. Phys. Lett. 101, 092109 (2012). [3] Z. Taghipour, V. Dahiya, T. Grassman, J. M. Fastenau, A. W. K. Liu, D. Lubyshev, S. Krishna, Proc. of SPIE, Vol. 11129, Infrared Sensors, Devices, and Applications IX; 1112905 (2019).

Welcome!

Partha Dutta (ACCGE), **Mike Dudley** (ACCGE)

Keywords:

Unlocking the AlN-based technology through crystal growth and epitaxy

Zlatko Sitar (North Carolina State University), **P. Reddy, R. Kirste, R. Collazo**

Keywords:

Single crystal aluminum nitride with a direct bandgap of 6.1 eV brings about technological opportunities to realize deep UV optoelectronics, extreme RF and power devices in addition to being a possible host for quantum interaction. Chronologically, the challenges and progress in AlN can be divided into three larger topics: crystal growth, epitaxy, and property control. Any crystal growth from the vapor phase is challenging and relies on one of the two strategies to achieve large-area wafers: growth of thick layers on non-native seeds and subsequent seed removal, or gradual crystal-size expansion through an iterative re-growth process. The latter was achieved in AlN through a scalable, iterative re-growth process in which the volumetric defect formation was suppressed and high crystal quality was maintained over generations of boules.
With the dislocation practically absent in the AlN substrates, surface morphology in homoepitaxy can be controlled from 2D nucleation to step flow growth and even layer-by-layer growth. The growth process is quantitatively described by an all-inclusive surface kinetic framework that connects input vapor supersaturation, surface supersaturation, surface diffusion length, and substrate misorientation angle. Management of surface steps is crucially important for growth of ternary alloys and doping. Historically, the conductivity in AlN has been very limited, presumably due to a DX transition forming an acceptor state and subsequent self-compensation, which imposed a severe upper limit on the achievable free carrier concentration. However, recent results show that the transition represents an equilibrium thermodynamic transition from a shallow to a deep donor state, which can be kinetically inhibited and the donor stabilized in its shallow state.
This presentation will give a historic perspective and present state-of-the-art and future development of the AlN-based technology.

Frontiers in Selective Area Growth, Etching, and Doping of GaN by OMVPE

Jung Han (Yale University)

Keywords:

Selective area growth (SAG) is a phenomenon in thin-film deposition where the sample surface is masked by a dielectric or refractory layer such that growth takes place only in exposed window regions. The selectivity is introduced due to large disparities in incorporation energetics and kinetics between the mask and window region. SAG was first discovered around 1965 in the study of GaAs. Its utility and popularity passes through cycles; in the 80s the lateral growth of silicon represented the earliest attempt of preparing silicon-on-insulator (SOI) structures, and in the 90s the lateral growth of GaN contributed to dislocation reductions for long-lifetime laser diodes. In recent years, we have witnessed the combination of SAG with nanoscale lithography for controlled synthesis of quantum and nano-structures. Because of the interest in GaN power electronics, there has been a growing interest in the past 10 years in developing selective area doping (SAD) of GaN in order to achieve lateral junction devices, where the most promising method is through selective area etching (SAE) followed by SAG. In this process, one particular need is to achieve a damage-free etch-and-regrowth interface. In this talk we will review several topics related to SAG, SAE, and SAD that have been investigated at Yale. In the area of SAG, we will discuss two novel epitaxial processes, one called orientation-controlled growth, and the other evolutionary selection growth. Concerning the important task of SAD and SAE of GaN, we will discuss a novel in-situ etching process during OMVPE toward selective-area etching. Instead of using the conventional ICP etching, tertiarybutylchloride (TBCl) is employed as an in-situ chemical etchant of GaN in MOCVD to create smooth trenches, and to remove plasma etching-generated damages on the surface. We will also describe our most recent effort in bypassing the constraint of dielectric masking during the in-situ etching, and to perform maskless selective area etching (SAE) to form low-defect lateral p-n junctions for GaN power electronics. The SAG work was supported by the U.S. DOE, Office of Basic Energy Sciences, MSE, under DE-SC0001134 monitored by Dr. Bonnie Gersten. The SAD and SAE work is supported by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. DOE, under DE-AR0000871 as part of the PNDIODES program managed by Dr. Isik Kizilyalli.

Bridgman Crystal Growth on Earth and in Microgravity

Aleksander Ostrogorsky (Illinois Institute of Technology)

Keywords: Growth; Bulk; III-Vs (Traditional), Ge, InI; Melt Growth; Narrow Semiconductor

Bridgman growth is the oldest method for crystal growth from the melt. On Earth, it is used because of its simplicity, low equipment and labor cost. In space laboratories, it is the only method used for melt-growth. The most important characteristic of the Bridgman process is that the solid-liquid (S-L) interface is in a continuous contact with the crucible, along the solid-liquid-crucible intersection, where spurious nucleation is likely to occur [1]. The concave interface promotes spurious formation of defects. The shape of the interface depends on: the furnace temperature profile, the thermal conductivity of the nearby materials, the growth rate, and the direction and intensity of the melt flow. The thermally-driven convection is a key controlling factor in all melt-growth processes [2]. Thus, in 1983, Don Hurle raised the question: ?Can we control or modify the flows to improve crystal properties?? Since on Earth the natural convection is unavoidable, the initial goal of the crystal growth experiments conducted in microgravity was to eliminate buoyancy driven flows. In the first part of this talk, we will review the results and conclusions, including our data obtained at SUBSA facility at the International Space Station (ISS). On Earth, forced convection as practical alternative to the less reliable option of completely eliminating thermally-driven flows. The general goal is to minimize the magnitude of natural convection relative to forced convection, which is steady and easy to control. Several techniques that have proven to be successful in improving melt flows including: the accelerated crucible rotation technique (ACRT), the traveling magnetic fields (TMF), coupled vibrational steering (CVS), and using a rotating baffle to drive the flow while simultaneously reducing natural convection. Virtually any level and path of forced convection will help to stabilize and homogenize the melt. Yet, the S-L interface remains difficult to control. Baffles are flow-directing or obstructing devices. In vertical Bridgman (VB) melts, the role of the baffle is to minimize the natural convection while driving forced convection [3]. The Schlichting?s ?Boundary layer theory? presents handful of flows for which the Navier-Stokes equations are solvable. Among these flows, two appear in Czochralski melts: i) the flow driven by the rotating disk and ii) the rotating flow near the ground. In general, disk-driven flows are optimal for various scientific and engineering applications because the boundary layers at the disk surface are uniform. Recently, we have demonstrated that both baffle and crucible rotation generates CZ-like flows in VB melts. [3,4]. Natural convection can be made negligible in production size melts. Using an low thermal conductivity baffle helps to flatten or make convex the S-L interface [3,4]. A slightly convex S-L interface can be achieved by selecting the optimal rotational rates and baffle material. [1] J.C. Brice, The Growth of Crystals from the Melt, North Holland Co., Amsterdam, 1965. [2] D.T.J. Hurle, J. Cryst. Growth 65 (1983) 124?132. [3] A. Ostrogorsky, Prog. Cryst. Growth Charact. Mater. 67 (2021) 100512. [4] N. Dropka and A. Ostrogorsky, Crystal Research and Technology 57 (2022) 2100251.

The development of ultrawide bandgap, pseudomorphic AlGaN semiconductor on native AlN substrates and its potential for opto-electronic and power devices (dedicated to Crystal IS co-founder Glen Slack)

Leo Schowalter (Lit Thinking, University of Central Florida, Cornell University, Nagoya University, Crystal IS)

Keywords:

High quality, 2-inch diameter AlN substrates have become widely available [1]. These substrates are produced by slicing bulk crystals of AlN that are grown through a process of high temperature sublimation of AlN polycrystalline material into Al and N2 vapor which is then recondensed onto a single crystal seed of AlN. While this form of crystal growth by physical vapor transport (PVT) is well known, the high reactivity of Al vapor and the stability of the N2 present unique challenges.

These single-crystal AlN substrates have enabled growth of Al1-xGaxN alloys which are pseudomorphically strained to match the lattice of the underlying AlN substrate despite the large mismatch in lattice parameters between AlN and Al1-xGaxN with increasing Ga concentration (x). As a result, threading dislocation densities well below 106 cm-2 are achieved which has allowed the development of superior performance electronic and optoelectronic devices such as UVC LEDs and laser diodes (LDs) at wavelengths shorter than 280nm. For instance, the low defect density enhances the radiative-recombination efficiency through the reduction of non-radiative recombination centers. In addition, the low extended defect density has made it possible to take advantage of distributed polarization doping. Most significantly, p-type Al1-xGaxN has now been demonstrated in high Al content Al1 xGaxN without the use of impurity doping. This breakthrough solved the critical problem of unacceptable resistivities in the doped layers with increasing band gap (particularly for p-type dopants). It appears that prior attempts to achieve distributed polarization doping of p-type Al1-xGaxN failed without the simultaneous use of p-type impurity doping due to the high density of threading dislocations present in Al1-xGaxN layers grown on foreign substrates such as sapphire.

Pseudomorphic growth and distributed polarization doping have made the achievement of new devices possible, such as the UVC laser diode [2]. These laser diodes open new possibilities for optical instruments which will benefit from very compact sources of radiation which are coherent and nearly monochromatic. It is also possible to precisely direct laser radiation in ways that simply are not possible for LEDs. As this technology develops, it may even be possible to achieve higher wall plug efficiencies than are achievable with UVC LEDs due to improved photon extraction efficiencies. However, the lifetime of these diodes (which operate at much higher current densities than LEDs) is still an important issue that needs to be addressed.

Preserving the low defect density of the highly strained pseudomorphic layers during device fabrication is also crucial to this technology. For instance, the side walls of mesa structures must be engineered to prevent the concentration of shear stress which will introduce dislocations [3]. I will also discuss the possibility of extending this technology to the development of far UVC laser diodes which would take advantage of the fact that the bandgap of Al1-xGaxN can go as low at 210nm as x goes to zero.

References: [1] J. Grandusky, et al. IWN 2022., [2] Z. Zhang, et al., APL (2022), 10.1063/5.0124480. [3] M. Kushimoto, et al., APL (2022), 10.1063/5.0124512

From Crystal Growth, to Entrepreneur, to Space Flyer

Greg Olsen (GHO Ventures)

Keywords:

Greg Olsen will review his history in the crystal growth community starting with epitaxial growth of metals and misfit dislocations in graduate school, followed by epitaxial growth and defect studies of III-V compound optoelectronic devices at CA Labs, and then on to two startup companies that made InGaAs detectors and imaging devices. After training in Russia for six months he flew to the International Space Station on a Soyuz rocket where he spent ten days. For the last 17 years Greg has been a venture capitalist, investing in a number of technology based businesses.

[AACG AWARD] Bulk Crystal Growth of Ternary III-V Compound Semiconductors – 30 years of personal journey

Partha S. Dutta (United Semiconductors LLC)

Keywords:

Modern electronic, photonic and fiber optic technologies have been made possible by III-V compound semiconductor materials and devices. Current device structures are based on epitaxial layers of ternary and quaternary compounds grown on binary substrates of GaAs, InP, GaP, InAs, GaSb and InSb. Some of the niche applications require bulk ternary substrates of different band gaps and lattice constants. However, the industrial crystal growth technology and optimized process parameters established for binary crystals cannot yield ternary crystals that are application worthy. This talk will discuss the fundamental challenges that have impeded the progress of ternary crystal growth. Defects such as cracks, inclusions, spatial compositional fluctuations are common in ternary crystals unless special processes are used during crystal growth. Some of the recent advances made to overcome these challenges during the growth of 50 – 150 mm diameter GaInAs, GaInSb, InAsP and GaInP bulk crystals using vertical gradient freezing (VGF) technique will be presented. The precise control of heat and mass transport in the melt during the crystal growth along with dopant incorporation strategies that are necessary during ternary crystal growth will be discussed. Specialized equipment developed for ternary crystal growth that requires precise gradient control for radial and longitudinal homogenous crystals will be presented.

Invited Talk

Potential Role of Reduced Gravity for Semimetal-Semiconductor Composite Bulk Crystal Growth and Novel Devices

Partha Dutta (United Semiconductors LLC)

Keywords: Growth; Bulk; Semiconductor-Semimetal; Melt Growth; Narrow Semiconductor; Magnetic Sensors

Semimetal-Semiconductor Composites (SSC) are a novel class of materials with limited number of research studies to-date yet offers unique characteristics for numerous large scale emerging applications including, magnetic sensing, thermoelectrics and photovoltaic power generation, quantum computing devices, components for energy storage systems, high performance optoelectronic and radiation detectors. For device fabrication, wafers with perfectly aligned and continuous nanowires embedded in the bulk crystals are necessary. Due to natural convection and buoyancy, crystals grown in terrestrial conditions (on earth) exhibit morphologies with non-uniform and randomly aligned nanowires. Microgravity condition provides the perfect environment for eliminating these detrimental effects, thus enabling large scale production of semiconductor composite crystals with desirable morphology. This talk will present some of the recent developments in terrestrial crystal growth of SSC as InGaAs-ErAs and InSb-NiSb at United Semiconductors LLC (USLLC). The potential role of microgravity on the microstructure of the grown crystals and its impact on magnetic sensor performance will be discussed. Based on preliminary analysis, it is anticipated the figure of merit (FOM) of the devices fabricated using space grown crystals could improve by a factor of 2-6 by virtue of uniform nanoscale/microscale wire morphology.

Characterization of Protein-based Artificial Retina Thin Films Produced via Layer-by-Layer Assembly on the International Space Station

Nicole Wagner (LambdaVision), **Jordan Greco** (LambdaVision), **Krishna Dixit** (LambdaVision), **Daniel Sylva** (LambdaVision), **Hope Sylva** (LambdaVision)

Keywords: Devices; Thin Film; Novel; protein layering; Energy Materials, Optical Materials, Sustainable Materials

LambdaVision has developed a protein-based artificial retina to restore vision to the millions of people blinded by retinal degenerative diseases, including retinitis pigmentosa and age-related macular degeneration. The artificial retina thin films are manufactured using a layer-by-layer (LBL) assembly technique, in which alternating layers of the light-activated protein, bacteriorhodopsin (BR), and a polycation binder are deposited onto an ion-permeable film. The resulting artificial retina thin films contain hundreds of oriented layers of BR, and upon the absorption of light, the thin films generate a unidirectional ion gradient that can stimulate the remaining neuronal network of the retina for patients suffering from advanced retinal degeneration. Despite early proof of concept work that demonstrated implant activity and effectiveness of stimulating retinal ganglion cells of degenerated retinal tissue, LBL production of the artificial retina thin films requires optimization to ensure consistency in thickness, homogeneity, and protein orientation. A microgravity environment is known to improve the three-dimensional assembly of thin films due to the elimination of buoyancy-driven convective turbulence and Stokes sedimentation effects. To date, LambdaVision, along with implementation partner, Space Tango, have completed a series of seven microgravity experiments on the International Space Station (ISS) that have established the hardware and software required for producing artificial retinas using a LEO platform. These experiments demonstrated the fluidics, operational controls, and in-process quality measurements were validated through the assembly of multiple artificial retina thin films in microgravity. These missions have demonstrated reproducible hardware performance in both a terrestrial and microgravity environment, and the CubeLabs have a proven tech stack with good control and automation. We have consistently met the goal of assembling 200-layer thin films in microgravity, and have also strengthened thin film quality assessment techniques using confocal microscopy, thus enabling the direct comparison of terrestrial- and microgravity-assembled artificial retinas films. Specifically, confocal microscopy was used to examine the thickness of the multilayered films, the extent of uniformity across the film, and the degree of aggregate deposition. Despite some midline shearing, the LBL assembly of the thin films was successful and validated the hardware and software required for production in the closed-loop CubeLab architecture. These advancements place LambdaVision and Space Tango in a favorable position for further microgravity tests, scaling up the production capabilities, and implementing GMP procedures for preclinical and clinical efforts.

An AI predictive platform for microgravity innovation

Ioana Cozmuta (G-SPACE Inc), **Dr. Remus Osan** (G-SPACE Inc), **Dr. Brian Motil** (G-SPACE Inc), **Dr. Christianna Taylor** (G-SPACE Inc)

Keywords: Defects, Modeling; Bulk, Thin Film; III-Vs (Traditional), ZBLAN, Oxides; Energy Materials, Optical Materials, Quantum Materials, Scintillator Materials, Sustainable Materials

Companies that use space in their product innovation are forecasted to establish new revenue growths between $0.4Bn and $4.2Bn [McKinsey, Microgravity Manufacturing, 2022]. Microgravity manufacturing refers to the process of manufacturing superior and/or unique products in outer space targeting applications on terrestrial markets in a variety of industry verticals such as semiconductors, fiber optics, pharma, biotech, food, agriculture, etc. It leverages a combination of factors such as vacuum, ultra-low temperatures, and finally microgravity, a six orders of magnitude reduction in one of the fundamental forces, gravity. Without gravity, there is no preferential axis which means that sedimentation and buoyancy-driven convection are inexistent. Some of the biggest challenges of microgravity manufacturing are: 1. Lack of convincing evidence for the terrestrial private sector related to microgravity product superiority and uniqueness; 2. Significant upfront costs related to flying payloads to space despite falling prices per lb to LEO; 3. High-risk profile due to long development timeliness via trial-and-error flights. To date, microgravity products are designed and optimized on a trial-and-error basis leading to a costly and inefficient process. Typically, data collected from microgravity experiments have been processed and analyzed postflight requiring repeated flights and lengthy cycles before obtaining tangible results. In addition, many experiments lack terrestrial ground control. Without a reference, quantifying the impact of microgravity on materials and processes can be challenging. In this talk, G-SPACE, Inc. will describe the development of an integrated AI-predictive platform for microgravity innovation. The curated microgravity datasets help visualize and predict microgravity performance and ensure an optimized performance envelope prior to flight. The platform can scan terrestrially through hundreds of thousands of formulations and identify those underlying unique microgravity materials. The AI/ML models enable improved quality control and in-space real-time analytics for monitoring the microgravity process and turning it into powerful predictive tools. By leveraging such tools, customers can better manage and even remove uncertainties due to microgravity. Between real-time analytics and prediction, the unique microgravity platform that G-SPACE is building will help maximize the value from the data collected in space, drive towards standardization, process control, and increase the safety of space operations. The goal is to achieve a 10X faster proof for microgravity products, cost savings through design and optimization prior to flight, and an overall lower risk, accelerating the timeline to commercialization of a variety of microgravity products for in-space manufacturing.

Invited Talk

Solution convection and the nucleation precursors in protein condensation.

Peter Vekilov (University of Houston)

Keywords:

TBD

Commercial Space Platform for Crystal Growth

Divya Panchanathan (Axiom Space)

Keywords: Defects, Growth, Technology/Equipment; Bulk, Thin Film; Carbides, III-Vs (Traditional); CVD, Gel Growth, Melt Growth, Solution Growth; Nonlinear, Scintillator, UWBG/WBG Semiconductor; Energy Materials, Optical Materials, Quantum Materials, Scintillator Materials

The commercial space economy is rapidly expanding and creating opportunities for â€˜future cities in spaceâ€™ where we will live and work off the planet. Axiom Space is leading the way by building the worldâ€™s first commercial space station, with a first module attached to the International Space Station (ISS) in 2025 that provides crew living quarters, external and internal payload capabilities, and state-of-the-art science and manufacturing facilities. This offers innovation opportunities for industry and academic researchers to perform applied research that leads to manufacturing of advanced materials in the low-Earth orbit (LEO) for electronics, energy, and biomedical applications. Microgravity offers a unique environment to grow crystals in ways that cannot be accomplished on Earth. Changes in fluid behavior such as the lack of buoyancy driven convection and sedimentation in microgravity lead to beneficial characteristics in materials like semiconductor crystals, 2D materials, and photonic materials, and macromolecule crystals. Some demonstrated benefits of the microgravity environment include the ability to isolate and study non-gravitational phenomena, preparing defect-free crystals, diffusion-driven manufacturing, and containerless processing of materials. This talk will highlight: (1) the Axiom station and its capabilities; (2) path towards commercial in-space manufacturing; and (3) on-going collaborations in crystal growth.

Crystal Growth in the SUBSA furnace in MSG: 2002 to 2022

Aleksandar Ostrogorsky (Illinois Institute of Technology), **Martin Volz** (MSFC, NASA), **Arne Croel** (U. Alabama Huntsville)

Keywords: Growth; Bulk; III-Vs (Traditional); Melt Growth; Narrow Semiconductor

In 2002, the investigation â€œSolidification Using a Baffle In Sealed Ampoules (SUBSA)â€□ was the first investigation to utilize the Microgravity Science Glovebox (MSG) Facility on the International Space Station (ISS). The SUBSA furnace was designed for growth of indium antimonide. It features a transparent section, which allows a side view of the melt, the solid-liquid (SL) interface and the growing crystal. In 2002, four Te-doped and three Zn-doped InSb crystals were grown in microgravity. Subsequently, the SUBSA furnace was used in several materials science investigations, including growing the radiation detector materials, InI and Cs2LiYCl6:Ce from the melt and vapor phase (2017 to 2019) and â€œBrazing of Aluminum alloys in Space (BRAINS)â€□. A review of the SUBSA furnace features and parameters will be presented, including the design of the growth ampoules, charge preparation, and the procedures used to grow InSb (in 2002) and InI (in 2019).

Detached Melt and Vapor Growth of InI in SUBSA hardware

Vladimir Riabov (Illinois Institute of Technology), **Aleksandar Ostrogorsky** (Illinois Institute of Technology), **Martin P**. **Volz** (MSFC NASA), **Arne Croell** (U. Alabama, Huntsville)

Keywords: Growth; Bulk; InI; Melt Growth; UWBG/WBG Semiconductor

Indium iodide (InI) single crystals, grown by the Bridgman process, have shown a significant promise as room temperature detector material for X-rays and Î³-rays due to the large, close to ideal, bandgap of Eg = 2 eV, and high electrical resistivity. Yet the transport properties of the charge and the detector performance remain inadequate. The Bridgman growth of semiconductor crystals in microgravity have typically resulted in partial dewetting and Marangoni convection, which disturbed the diffusion-controlled growth and produced nonuniform dopant distribution. However, unconfined or partially confined solidification drastically reduced the number of stress-induced defects compared to the confined growth in crucibles on Earth. The goal of the present investigation was to explore melt growth of a heavy metal halide in microgravity, focusing on dewetting, in order to improve the crystalline perfection, i.e., to reduce the number of stress-related defects. InI was chosen because it is non-toxic and has a low melting point of only 365 C (~150 C below the melting point of InSb, used in the SUBSA experiments in 2002). Furthermore, InI melts and evaporates congruently, making it suitable for both growth by directional solidification and growth from the vapor phase. In preparation for the flight experiments, ground-based experiments were conducted in the SUBSA ground unit, consisting of 4 melt growth and 2 vapor growth experiments. The crystals were grown by a gradient freeze method by lowering the setpoint of the furnace. The transparent section of the SUBSA furnace did not allow observations of the solid-liquid interface. Contrary to our expectations, the possible occurrence of dewetting during growth could not be observed. We will present i) the ampoule design and preparation, ii) the experiments conducted in the SUBSA ground unit, iii) the images obtained during the microgravity experiments and iv) the results of the characterization of the grown crystals and detector fabrication.

Invited Talk

Advancements in Numerical Modeling of Epitaxy of Electronic Materials

Alex Galyukov (STR US, Inc.)

Keywords: Growth, Modeling, Technology/Equipment; SiC, single-crystal diamond, Silicon; CVD, MPCVD; Narrow Semiconductor, UWBG/WBG Semiconductor; Energy Materials

The advancement of computer technologies has enabled numerical modeling to evolve into a powerful practical tool for the semiconductor community. Simulations have become an integral part of multiple levels of today's device manufacturing cycle. In this talk we want to highlight the modeling capabilities and applications that were out of reach just a few years ago. We will focus on three technologies: chemical vapor deposition (CVD) of silicon, CVD of silicon carbide, and microwave plasma activated chemical vapor deposition (MPCVD) of diamond. Since CVD Si is a seasoned technology, achieving further improvements requires meeting extremely high standards of uniformity for deposition on large wafers with typical diameter of 300 mm. The complexity of the equipment, which includes multiple inlets and an intricate configuration of heating and reflecting elements, makes both experimental process optimization and modeling of these systems particularly challenging. Recently developed capabilities of 3D heat transfer modeling with conjugated simulation of lamp heating, specular reflection from curved surfaces, absorption and refraction of radiant heat by quartz in a reactor with multiple heating zones both above and below the susceptor, made it possible to significantly increase the accuracy of simulations. In the case of CVD SiC, thermal simulations are relatively straightforward, but the chemical model is quite complex and computationally demanding. SiC is a binary compound and precursors for Si and C undergo different chemical transformations before they can be utilized at the wafer with about twenty chemical components that should be considered to cover all necessary volume and surface reactions. Moreover, practically all involved chemical processes are highly sensitive to temperature. Besides, both quality of the layers and doping incorporation depend on the C/Si ratio of the gas mixture near the substrate. Presented are the results of conjugated 3D simulations of heat transfer, flow, and chemical reactions during CVD SiC. Finally, simulations that can be useful for mitigating non-uniformity of the single crystal diamond (SCD) growth rate in CH_4/H_2 MPCVD reactors, need to include modeling of localized microwave plasma with associated temperature and reactive species distributions in presence of complex mechanisms of volumetric and surface chemical reactions. In this work, we present simulation results of SCD deposition rate and uniformity over the substrate area in a conventional MPCVD reactor design for various process conditions such as absorbed microwave power and gas pressure. We demonstrate the significant role of substrate holder features on radical flux and, thus, growth rate.

Invited Talk

Growth of 2H-SiC pure hexagonal polytype by using nucleating agents

Narsingh Bahadur Singh (University of Maryland Baltimore County)

Keywords: Growth; Carbides, Nitrides; CVD, PVT; UWBG/WBG Semiconductor

There is a strong need for hexagonal and lattice matching high thermal conductivity substrate for the growth of gallium nitride. Tremendous progress has been achieved in developing substrates, however thick films of GaN grown on 6H-SiC and 4H-SiC substrates have shown variety of defects due to different crystal symmetry. This problem can be solved by growing of SiC doped with AlN with hexagonal symmetry (2H-SiC) without compromising thermal conductivity. Experiments show that material nucleates as discs before coalescing to become a continuous layer. 2H is the natural crystal orientation of AlN, and so the transition from 6H- to wurtzite also aids good crystal quality. We observed that impurities significantly alter the nucleation. The well-developed discs are generally of the order of 100ï□m and exhibit flat [0001] surface. The screw dislocations provide the steps for the growth which starts as a flat top hexagonal pyramid merging together as continuous layer. Details of characterization by XRD, SEM, TEM and other methods for the thick SiC on thick AlN film and SiC-AlN film showed 2H- structure. XRD of some thick films showed full width of half maxima with 1500 arcsecond.

Analysis of strain due to High Energy Ion Implantation by Synchrotron X-ray Topography

Zeyu Chen (Stony Brook University), **Yafei Liu** (Stony Brook University), **Qianyu Cheng** (Stony Brook University), **Shanshan Hu** (Stony Brook University), **Balaji Raghothamachar** (Stony Brook University), **Reza Ghandi** (GE Research), **Stacey Kennerly** (GE Research), **Michael Dudley** (Stony Brook University)

Keywords: Characterization, Defects, Devices; Thin Film; Carbides; CVD, ion implantation, PVT; UWBG/WBG Semiconductor; Energy Materials

4H-SiC high voltage devices, which can withstand 1.7 to 6.5 kV, are highly sought for applications, such as hybrid, shipboard and power grid systems, and high-speed trains. Usually, such medium or high voltage devices are fabricated on 4H-SiC wafers with thick epilayer that can increase the breakdown of the device [1]. However, doping such thick epilayer is quite challenging. An optimized solution of selective area doping is utilizing multi-steps high energy ion implantation system. Such a system has been developed at the Tandem Van de Graaff accelerator facility at Brookhaven National Laboratory with the capability of multi-steps high energy implantation at energies up to 150 MeV [2]. By employing such a system, medium voltage charge balance devices and 2 kV superjunction structure PIN diode have been demonstrated [3-4]. The lattice damages induced by the implantation were primally characterized by Synchrotron X-ray Topography where the X-ray with energy of 8 keV is initially monochromatized by double crystal Si (111) monochromator followed by tuning with an asymmetric Si (331) beam conditioner. The effective width of the resultant X-ray beam is lowered to 0.5â€□ due to the asymmetric factor of the beam conditioner [5]. Therefore, the angular resolution is vastly enhanced, enabling miniscule distortions in the lattice to be detected. Using the 4H-SiC (0008) reflection the d spacing of which is matched to that of the Si (331) conditioner, the final rocking curve width of the sample is almost the same as its intrinsic Darwin width (2.4 Ê¹Ê¹). Multiple asymmetric diffraction peaks with an angular separation of only 2â€□ (arcseconds) were shown in the topographs, indicating inhomogeneous strain distribution across the implanted layer. The strain profile of the implanted layer was obtained by Rocking-curve Analysis by Dynamical Simulation (RADS).

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Invited Talk

Gallium Oxide Bulk Crystal and Substrates Technology.

Akito Kuramata (Novel Crystal Technology, Inc.)

Keywords: Growth; Bulk; Oxides; Melt Growth; UWBG/WBG Semiconductor; Energy Materials

Ga_2O_3 is expected as a material for next generation power devices. Since it has a large breakdown electric field, it is suitable for high breakdown voltage applications over 3 kV. It is a material that can be produced at a lower cost than SiC and GaN because it can be melt-grown and its hardness is not high. Currently, 100-mm substrates manufactured by the EFG method are commercially available. A 100-mm epi-wafer with a carrier concentration of 10^{15}-10^{17} cm^{-3}, grown by the HVPE method, has also been commercialized. However, there are no commercial Ga_2O_3 devices yet while research is progressing. So far, SBDs and FETs have been demonstrated with ampere-class currents and breakdown voltages of 1 kV or higher. The availability of native substrates is the most important feature of gallium oxide when considering power device applications. In this presentation, we will report on two bulk growth techniques. One is the growth of large n-type crystals by the edge-defined film-fed growth (EFG) method. Another is the growth of 2-inch high-resistance crystals by the Vertical Bridgman (VB) method.

Invited Talk

Materials and Device Engineering for High-Performance Gallium Oxide Electronics

Siddharth Rajan (The Ohio State University), **Sushovan Dhara** (The Ohio State University), **Ashok Dheenan** (The Ohio State University), **Nathan Wriedt** (The Ohio State University)

Keywords: Devices, Growth; Oxides; CVD, MBE

The unique material properties of Gallium Oxide make it promising for a range of future applications, but innovative materials and device engineering are needed to translate these ultimate material limits to real technology. This presentation will discuss our recent work on epitaxy, heterostructure design, and electrostatics to achieve high-performance Image-Ga2O3 devices. Recent work on lateral Gallium Oxide transistors have demonstrated excellent electron transport and device characteristics. We will discuss some advances in materials and device design for lateral structures which enabled key transistor demonstrations including the first Image-(Al,Ga)2O3/Image-Ga2O3 modulation-doped structures with excellent transport, high sheet charge density modulation-doped structures, and scaled delta-doped transistors with cutoff frequency of 27 GHz. The high breakdown field of Gallium Oxide makes it critical to manage electric field profiles within the device. Extreme-permittivity dielectrics provide unique opportunities to create devices that can sustain extreme fields without premature breakdown of metal-semiconductor and dielectric-semiconductor interfaces. We will discuss promising results related to this approach, such as BaTiO3/Ga2O3 heterojunctions that enable more than 5.7 MV/cm vertical breakdown field and BaTiO3/Ga2O3 transistors with > 5.5 MV/cm breakdown field, the highest for a field effect transistor in any material system. Significant potential exists for vertical Gallium Oxide devices. In this talk, we will discuss out work on achieving vertical Gallium Oxide devices with enhanced field and dielectric engineering. We will outline the use of a new damage-free epitaxial etching technique using Ga atomic flux that enables highly precise fabrication of structures, and the integration of high field-strength dielectrics. We will discuss the development of vertical trench Schottky diodes with excellent electric field strength (>5 MV/cm) and figure of merit (>2 GW/cm2) using these methods.

Epitaxy and Engineering of beta-Ga2O3 Devices for High-Voltage Applications

Sriram Krishnamoorthy (Materials, University of California, Santa Barbara), **Arkka Bhattacharyya** (Materials, University of California, Santa Barbara), **Saurav Roy** (University of California, Santa Barbara), **Carl Peterson** (University of California, Santa Barbara)

Keywords: Devices, Growth; Thin Film; Oxides; CVD; UWBG/WBG Semiconductor; Energy Materials, Sustainable Materials

This work focuses on growth, doping, epitaxial stack engineering, and characterization of Î²-Ga2O3 thin films, device designing, fabrication, and demonstration of high voltage (VBR) and high field strengths in Î²-Ga2O3 based high-performance devices and explores the potential and limitations of this emerging UWBG Ga2O3 materials system. We demonstrate a hybrid low temperature - high temperature (LT-HT) buffer/channel stack growth using MOVPE with record carrier mobility values (range of 196â€“85 cm2/Vâ‹…s) over four orders of doping range (2e16 â€“ 1e20 cmâˆ’3). Record electron mobility of 110 cm2/Vs is also demonstrated in delta-doped (2D) channels (ns = 9.2e12 cm-2). The improvement in transport properties was achieved mainly by realizing pristine doped channels, eliminating undesired parasitic conduction paths, and minimizing carrier compensation. Lateral transistors utilizing these uniformly Si-doped channels with LT buffers exhibit state-of-the-art device performance. Planar and tri-gate transistors showed very low reverse leakage for breakdown voltages up to 3 kV. Due to enhanced electron mobility, these devices were able to exhibit low on-state resistances for a given device dimension. In conjunction with effective electric-field management (achieved max average breakdown field of over 4 MV/cm with tri-gate architectures), these devices were able to deliver a high power figure of merit of âˆ¼1 GW/cm2, setting a new record for Ga2O3 transistor device technology. The Ron.Qg switching figure of merit was also estimated in these planar and tri-gate Ga2O3 transistors, where the upper-bound value for gate charge is estimated using full drift region depletion and field plate capacitances were calculated using parallel plate approximations. Upper-bound RonQg product of < 1000 mâ„¦.nC for our ~1.2 kV class transistors were estimated - showing significantly improved performance over Si SJ-MOSFETs (COTS), SiC MOSFETs (COTS), current Ga2O3 FETs (SOTA) devices and comparable performance to GaN HEMTs (COTS and SOTA). With fundamental advantages which offer high breakdown strength, our material growth and device demonstrations using MOVPE show pathways for achieving epitaxial films with exceptional transport properties and designing next-generation medium-to-high voltage Ga2O3 low-loss power devices.

Recent advances in epitaxial growth, in-situ etch, and regrowth of beta-Ga2O3 films using MOVPE

William Brand (Agnitron Technology), **Fikadu Alema** (Agnitron Technology), **Andrei Osinsky** (Agnitron Technology)

Keywords: Growth; Thin Film; Oxides; VPE; UWBG/WBG Semiconductor; Energy Materials

Î²-Ga2O3 has recently become the focal point of semiconductor research for application in power electronics due to its large bandgap of ~ 4.9 eV, estimated high breakdown field of ~ 8 MV/cm, and availability of melt grown high quality Î²-Ga2O3 substrates. The growth of high-quality epitaxial Î²-Ga2O3 films with low dislocation density and background impurities on top of native substrates is critical to realize high-performance power electronic devices. Among the available epitaxial techniques, metal organic vapor phase epitaxy (MOVPE) has proven suitable for producing high-quality epitaxial Î²-Ga2O3 films at a fast growth rate with controllable doping [1]. In this work, we will present recent advances in epitaxial growth, in-situ etch, and regrowth of Î²-Ga2O3 films using MOVPE. The use of triethylgallium (TEGa) and trimethylgallium (TMGa) as Ga precursors for the growth of high-purity, carbon-free, epitaxial Î²-Ga2O3 films will be examined. High-purity homoepitaxial Î²-Ga2O3 films with low-temperature (LT) electron mobility ranging between 10,000 cm2/Vs and >23,000 cm2/Vs, and acceptor concentrations as low as 2Ã— 1013 cm-3 have been demonstrated using the two Ga precursors [2, 3]. This high LT e-mobility obtained from MOVPE Î²-Ga2O3 is >8Ã— and >4Ã— higher than the best values reported by MBE and by HVPE, respectively, and is ~2-3Ã— higher than the state-of-the-art LT mobility values of the best SiC and GaN bulk films [2, 4]. Critical process conditions and MOVPE reactor geometries required to obtain such highly pure Î²-Ga2O3 films will be discussed. In this talk, we will also present on in-situ Ga-based etching of Ga2O3 in MOVPE using TEGa or TMGa as Ga precursors, followed by a regrowth process. The effect of various etch parameters, such as TEGa or TMGa flow rates, substrate temperature, substrate orientation (001) and (010)), and reactor pressure on etch rate and surface roughness will be discussed. An etch rate of >8.0 Î¼m/hr with RMS roughness of ~2.5 nm was demonstrated by flowing ~140 Î¼mol/min TEGa. The use of tertiarybtylchloride (TBCl) for in-situ removal of Ga metal deposits from the etched Î²-Ga2O3 surface will be discussed. In-situ etch followed by regrowth led to defect-free interfaces as compared to that of plasma-etched regrown structures. 1] F. Alema, Journal of Crystal Growth 475, 77 (2017). [2] G. Seryogin, Appl Phys. Lett. 117, 262101 (2020). [3] F. Alema, APL Materials 7, 121110 (2019) [4] F. Alema, Compound Semiconductor Mag. 28, 16 (2022).

Invited Talk

Large Diameter 4H-SiC Growth and Defect Characterization Methods

Robert Leonard (Wolfspeed, Inc.), **Yuri Khlebnikiov** (Wolfspeed, Inc.), **Adrian Powell** (Wolfspeed, Inc.), **Caleb Kent** (Wolfspeed, Inc.), **Michael Fusco** (Wolfspeed, Inc.), **Matthew Conrad** (Wolfspeed.com), **Varad Sakhalkar** (Wolfspeed.com), **Edward VanBrunt** (Wolfspeed.com), **Elif Balkas** (Wolfspeed.com)

Keywords: Characterization, Defects, Growth; Bulk; Carbides; PVT; UWBG/WBG Semiconductor; Energy Materials, Quantum Materials

The continuing advancement of state-of-the-art SiC substrates is fueling the transformation to electric vehicles by enabling high power devices, where traditional silicon devices would fail. Successful crystal growth of SiC depends on the ability to produce high quality wafers with very few device limiting defects, and to produce them at a volume to sustain the market. We will give an overview of PVT SiC crystal growth and the quality requirements of wafers produced from these crystals. SiC has many potential polytypes, therefore requiring a very stable growth process to produce the desired 4H-SiC polytype. Any deviation in the growth is likely to cause unwanted defects. Typical defects are superscrew threading dislocations (micropipes), foreign and polytype inclusions, and elementary dislocations. By tightly controlling the growth parameters, we have been successful in producing industry leading substrates for power and RF devices. We currently produce commercially available 150 mm 4H SiC n-type and semi-insulating substrates, and have both demonstrated and are developing our production 200 mm single-crystal 4H-SiC substrates used in the first 200 mm SiC device fab in the world. Further, we will show our advances in characterizing the resulting wafers with non-destructive techniques, allowing for feedback in the growth of 4H-SiC crystals and ultimately leading to improved and reliable device performance. Increased device yield and manufacturing efficiency require continual feedback of extended defects, relying on consistent and high throughput detection methods. We are moving from traditional destructive etch methods to non-destructive methods for defect detection. This allows the ability to determine performance on the same material that is characterized, as well as reducing the waste and hazards associated in characterizing SiC. Defect information feedback for both success and failure, from crystal growth through device fabrication, is key to process improvement.

Invited Talk

The research and industrialization of SiC substrate in China

Yan Peng (Shandong University), **Xianglong Yang** (Shandong University), **Xiufang Chen** (Shandong University), **Xuejian Xie** (Shandong University), **Xiaobo Hu** (Shandong University), **Xiangang Xuï** (Shandong University), **Yaohao Wang** (Guangzhou Summit Crystal Semiconductor Co)

Keywords: Growth; Bulk; Carbides, Silicon Carbide; PVT; UWBG/WBG Semiconductor

SiC is characterized by its exceptional electrical properties and its high thermal conductivity, such as wide band gap, high breakdown electric field and high electron saturation velocity. The devices based on SiC materials give rise to high efficiency and low-cost system, not only operate at higher temperature, but also have higher reliability at high voltage and high frequency. For SiC based high-power device supply chain, research and industrialization of high-quality and large-size wafer is current focus. In the past 20 years, advances in the growth and processing technology for SiC substrate in China has resulted in the industrialization of 2-6 inch and the research of 8 inch SiC substrates. The state of art of research and industrialization and existing challenges are discussed in this study. With self-made equipment and unique design growth chamber for diameter enlargeï¼Œ the growth of 200mm SiC has made a practical reality. Crack-free high quality 200 mm 4H-SiC crystal is obtained using PVT under the optimized temperature distribution. The whole area of the wafer is 4H-SiC measured by Raman spectrum mappingï¼ŽThe rocking curves of X-ray shows that the average full width at half maximum of five points range from edge to the center of wafer is 32.7 arcsec. The resistivity of whole wafer is 20-23m Î© Â· cm and the non-uniformity less than 4%. The density of micropipe is 0.3cm-2 and that of TSD is below 100 cm-2. At same time, new Chinese substrate players, such as GZSC, are focusing on yield and quality improvements and pushing for expansion their capacity. However, the transition to 20mm SiC substrate faces main challenges such as high defect density and the control over the wafer bow/warp. It takes some time for transition from R&D to production and quality improvement.

Evaluation of thermal stress distribution in off-axis grown SiC crystals

Peter Muzykov (Onsemi), **Eugene Tupitsyn** (Onsemi), **Roman Drachev** (Onsemi), **Dean Skelton** (Onsemi), **Hrishikesh Das** (Onsemi), **Bhuvaragasamy Ravi** (Onsemi), **Honza Tesik** (Onsemi), **Jestin Johnston** (Onsemi)

Keywords: Defects, Modeling; Bulk; Carbides; PVT; UWBG/WBG Semiconductor; Energy Materials

New demand for SiC power devices insists on production of large diameter high quality SiC substrates. Mass production of devices with superior characteristics requires further improvement of SiC material quality and yield, as well as cost reduction. While the killer defects such a micropipes are mostly eliminated, the basal plane dislocations (BPD) and stacking faults (SF) are still present in SiC substrates and their reduction is of first importance to improve device performance. During growth of large diameter SiC crystals thermal stress develops during growth and cooling stages. Such stress is known to be one of the major factors that may cause BPD generation, wafer warpage or even boule cracking and its magnitude is expected to increase when the diameter of crystal increases from 6â€ to 8â€. In this work we studied thermal stress distribution in off-axis grown SiC crystals. We used numerical modelling to find correlation between stress and dislocation density in large 8â€ SiC crystals. Components of stress tensor were calculated for on-axis growth and then resolved shear stress was found for the primary and secondary slip systems in the crystals grown off-axis. Our results indicate that the shear stress along <11-20> in the basal plane of the off-axis grown crystals is asymmetric when the hoop stress is larger than the shear stress component. This suggests that BPD density may increase toward the opposite to the basal-plane-facet side of the boule. We also discussed the possibility of boule cracking based on the fracture toughness of the material.

Investigation of defect formation at the early stage of PVT-grown 4H-SiC crystals

Shanshan Hu (Stony Brook University), **Yafei Liu** (Stony Brook University), **Zeyu Chen** (Stony Brook University), **Qianyu Cheng** (Stony Brook University), **Balaji Raghothamachar** (Stony Brook University), **Michael Dudley** (Stony Brook University)

Keywords: Characterization, Defects, Growth; Bulk; Carbides; PVT; UWBG/WBG Semiconductor; Energy Materials

Silicon Carbide, typically 4H-SiC, due to its excellent electrical and thermal properties, has been replacing conventional silicon materials, which are considered to have reach their limit, for high power and high frequency applications[1]. Nevertheless, high quality SiC wafers with low defect density are still in urgent need for automotive and energy saving applications. SiC wafers are obtained from bulk growth by physical vapor transport (PVT) method and considerable efforts have been expended to optimize growth process to lower defect densities. One major approach is the study of initial stages of crystal growth as most defects are nucleated at this stage and propagate into the boule. Nucleation of threading edge dislocations (TEDs) and threading screw dislocations (TSDs) at the initial growth stage in PVT-grown SiC is revealed by Sanchez et al[2]. Behaviors of TEDs, TSDs/threading mixed dislocations (TMDs), and basal plane dislocations (BPDs) across the seed/newly grown layer interface in PVT-grown 4H SiC are demonstrated by Ailihumaer et al[3]. However, more detailed investigations are required for PVT grown 4H-SiC crystals during initial stage of growth. In this study, 4Â° off-axis 4H-SiC wafers with several hundred microns of initial-stage growth are prepared by PVT method. Synchrotron X-ray topography (SXRT) images for both seed and as-grown side of these initial-stage growth wafers reveals dramatically modified defect distribution across the seed/newly grown layer interface. The deflection of TEDs and TSDs/TMDs is observed to occur at the initial-stages of growth. Dislocations running along 11-20 directions on basal plane are observed to form rhombus shapes, suggesting the formation of Shockley stacking fault starting at initial stage of crystal growth. Prismatic slip is observed to take place near the wafer edges and prismatic dislocations undergo cross slip to form unique dislocation configurations.. A statistical analysis on defect changes across the seed/newly grown layer is being carried out and the results will be reported. These results will be complemented by observations from Nomarski optical microscopy (NOM) and Raman Spectroscopy studies to propose the formation mechanism of defects across the seed/newly grown layers.
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Invited Talk

Novel Graphene and SiC Epitaxy to Enable Film Transfer

Daniel Pennachio (US Naval Research Laboratory), **Jenifer R**. **Hajzus** (US Naval Research Laboratory), **Andrew C**. **Lang** (US Naval Research Laboratory), **Rhonda M**. **Stroud** (Former employee of US NRL, Current address: SESE ASU), **Rachael L**. **Myers-Ward** (US Naval Research Laboratory)

Keywords: Growth; Thin Film, 2D; Carbides; CVD; UWBG/WBG Semiconductor; Energy Materials, Quantum Materials

Remote epitaxy (RE) is a promising technique for epitaxial film transfer that utilizes graphene as a release layer [1]. Graphene grown on SiC(0001) substrates through Si sublimation or through propane chemical vapor deposition (CVD) is an ideal platform for remote epitaxy of wide bandgap (WBG) semiconductors as there is no need for a graphene transfer step, mitigating contamination or defects that can complicate the remote epitaxy process. In addition, the graphene/SiC materials system is compatible with commercially-viable WBG semiconductor growth and processing, making it a suitable choice for scalable future development. A challenge to utilizing SiC is that CVD growth is typically conducted using high-temperature hydrogen-based chemistries that could damage or remove graphene. This study investigates the effect of alternative low-H2 CVD growth conditions on SiC/graphene/SiC(0001) remote epitaxy that may reduce damage to the graphene barrier. In addition, graphene preparation and associated surface morphology is varied to explore its effect on SiC epilayer formation. For this work, the effects of Ar:H2 process gas flow ratio, growth precursor C/Si ratio, and growth temperature on hot-wall CVD SiC RE crystalline quality were investigated. Both semi-insulating nominally on-axis 6H-SiC(0001) and n-type 4Â° off-axis 4H-SiC(0001) substrates were used to produce different surface morphologies and graphene layer numbers. Nomarski optical microscopy, scanning electron microscopy, and atomic force microscopy found CVD deposition at 1620Â°C with Ar/H2 ratios <20/5 slm, and C/Si ratios <1.55 to have the smoothest surface morphology and fewest polytype inclusions. Substrates with offcuts <0.1Â° from SiC(0001) exhibited lower epilayer macrostep density, but showed evidence of polytype impurities and 3D growth at C/Si ratios > 1.0. RE on EG/4H-SiC(0001) substrates with a 4Â° off-cut from SiC[0001] had a wider parameter range resulting in single-crystalline growth compared to growth on the nominally on-axis substrates despite growth of >1 monolayer EG on these substrates. This study found smooth, single-crystalline polytype-pure SiC(0001) epilayers on EG substrates could be grown using predominantly Ar carrier gas, with H2 concentrations as low as ~2%. Through this study, optimal SiC RE growth conditions are suggested for a balance of EG survivability and SiC film morphology. [1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340â€“343 (2017).

Invited Talk

Electric and spin Hall transition in monolayer Fe3GeTe2

Gen Yin (Georgetown University)

Keywords: Defects, Modeling; Low Dimensional, Thin Film, 2D; Novel; Theory; Transport

As a two-dimensional (2D) magnet, Fe3GeTe2 (FGT) has a surprisingly robust long-range ferromagnetic order with a perpendicular easy axis and a reasonably high Curie temperature. Distinct from many 2D spintronic materials discovered recently, the family of Fe3,5GeTe2 are known as Ising itinerant 2D magnets, owing to their unique gapless spectrum and the sizable perpendicular anisotropy. Such anisotropy is a consequence of the strong spin-orbit coupling (SOC) given by the Te atoms, which also strongly impacts the transport behavior of carriers, resulting in a sizable anomalous Hall effect. However, such anomalous Hall effect is minimized in the case of a monolayer due to the missing of a nodal line perpendicular to the van der Waals plane protected by the symmetry of a bulk. In the case of a monolayer, the spin texture, the symmetry and the geometry of the Fermi surface are sensitive to the direction of magnetization due to the strong SOC. This enables intricate selection rules of spin-dependent scattering and transport. In this talk, I will demonstrate that the spin-dependent scattering in a monolayer FGT can work together with the van Hove singularities near the Fermi surface, resulting in a switching between anomalous Hall effect and spin Hall effect in a monolayer, even without the vertical nodal line. These Hall effects are allowed by an in-plane magnetization that breaks the atomic C3 rotation symmetry, which otherwise forbids any leading-order Hall effects for all individual bands. The transition between the electric and spin Hall effects is a plausible way to detect the switching of an adjacent insulating magnetic material with unknown magnetic order using carrier transport. This is particularly useful to detect the switching of an antiferromagnet (AFM) since the scattering selection rule is only sensitive to the orientation of the spins of the disorder, instead of the sign. The vast parameter space of stacking and twisting also enables the modulation of the transport and magnetic properties in a large range. These advantages make FGT an intriguing platform to investigate 2D magnetism as well as to implement next-generation low-dimensional spintronic devices.

Invited Talk

Towards Controlled Synthesis and Scalable Production of 2D Crystals

Jun Lou (Rice University)

Keywords: Fundamentals, Growth; 2D; Nitrides, TMDs; CVD; Narrow Semiconductor, UWBG/WBG Semiconductor; Energy Materials, Quantum Materials

The emergence of two-dimensional (2D) materials has captured the imagination of researchers since graphene was first exfoliated from graphite in 2004. Their exotic properties give rise to many exciting potential applications in advanced electronic, optoelectronic, energy and biomedical technologies. Scalable growth of high quality 2D materials is crucial for their adoption in technological applications the same way the arrival of high-quality silicon single crystals was to the semiconductor industry. A huge amount of effort has been devoted to grow large-area, highly crystalline 2D crystals through various methods. While CVD growth of wafer-scale monolayer graphene and TMDs has been demonstrated, considerable challenges still remain. In this talk, we first advocate for the focus on the crystal growth morphology as an underpinning for understanding, diagnosing and controlling the CVD process and environment for 2D material growth. Like snowflakes in nature, 2D crystals exhibit a rich variety of morphologies under different growth conditions. The mapping of crystal shapes in the growth parameter space â€œencodesâ €� a wealth of information, the deciphering of which will lead to better understanding of the fundamental growth mechanism and materials properties. However, the morphology pattern evolution of 2D crystals such as MoS2 monolayers under a practical CVD growth condition is highly complicated due to the entanglement of multiple growth factors. The ability to directly monitor it in real-time would be substantial to provide first-hand data to lay the groundwork for most advanced tools such as machine-learning to unravel those threads. A customized system with the function of observing and recording the CVD growth of MoS2 in a miniature furnace is developed. Image processing techniques are utilized to convert the real-time growth footage into frame-wise digital numbers and machine-learning is deployed to uncover the importance of multiple controlling factors in the growth. The model successfully guides the discovery of experimental control parameters to grow ultra-large size MoS2 monolayers. The model also demonstrates the possibility to trace back experimental condition by analyzing the crystal morphology parameters. In a parallel effort, we also demonstrate that the widely used powder-processing technique of dry ball-mill, can be improved to produce high-quality 2D flakes in large scale and with low cost. Seventeen types of commonly seen polymers, including both artificial and natural ones, have been examined as additive to dry ball-mill of hexagonal boron nitride. The potential of polymer-assisted ball-mill exfoliation as a universal way to produce ultra-thin 2D nanosheets is also demonstrated.

Invited Talk

Investigating the Magnetotransport Properties of Hydrogen and Magnesium Intercalated Graphene on Silicon Carbide.

Jimmy Kotsakidis (Laboratory for Physical Sciences), **Gregory M**. **Stephen** (Laboratory for Physical Sciences), **Matthew DeJarld** (U.S. Naval Research Laboratory), **Rachael L**. **Myers-Ward** (U. S. Naval Research Laboratory), **Kevin M**. **Daniels** (University of Maryland), **D**. **Kurt Gaskill** (University of Maryland), **Michael S**. **Fuhrer** (Monash University), **Aubrey T**. **Hanbicki** (Laboratory for Physical Sciences), **Adam L**. **Friedman** (Laboratory for Physical Sciences)

Keywords: Characterization, Devices, Growth; 2D; Silicides; Intercalation growth - 2D hetero-epitaxy; Narrow Semiconductor, Dirac Semimetal; Quantum Materials

The intercalation of graphene with foreign atoms or molecules can drastically alter the electronic properties of the graphene. For instance, hydrogen intercalated graphene results in conversion from n-type to p-type, and magnesium intercalated graphene results in a highly n-type doped (~1E14) graphene.[1][2] Magnetotransport results of highly n-type doped and intercalated graphene are rarely reported due to the air-sensitive nature of these materials. The graphene that is typically chosen for these experiments is epitaxially synthesized graphene on silicon carbide. In this system, the graphene is separated from the surface of the SiC by a carbon â€˜bufferâ€™ layer, that differs from the structure of graphene due to its covalent bonding with the surface of the SiC. Upon intercalation, the intercalant typically breaks the buffer layer-SiC covalent bonds; converting the buffer layer into another layer of graphene. In this talk, I will overview the intercalation process, before presenting magnetotransport results on hydrogen and magnesium intercalated graphene on silicon carbide. In the case of hydrogen intercalated graphene, I observe Shubnikov-de Haas (SdH) oscillations, which I use to determine key physical parameters such as the effective mass and SdH oscillation frequency, which permit calculation of the Fermi level. I compare this value with the value obtained from STS measurements, and explain why one cannot rely on just the Hall effect. Furthermore, we measure the quantum scattering time to find that charged scattering dominates in hydrogen intercalated graphene. This conclusion is also supported with scanning tunneling microscopy (STM) taken at 4.6 K. In the second part of the talk, I will present magnetotransport results on magnesium intercalated graphene. While highly n-type doped graphene (i.e., calcium intercalated) is typically unstable, Mg-intercalated graphene is semi-stable in ambient air on the order of ~6 hours, representing a unique opportunity to study the transport properties of highly n-type doped graphene. In the case of Mg intercalated graphene, I observe a clear weak anti-localization (WAL) peak that persists up to 1.5 K. The origins of this WAL peak will be explored. Furthermore, I observe a clear switching from negative to positive magnetoresistance which I attribute to impartial intercalation. [1] Kotsakidis, Jimmy C., et al., Chemistry of Materials 32.15 (2020): 6464-6482. [2] GrubiÅ¡iÄ‡-ÄŒabo, Antonija, Kotsakidis, Jimmy C., et al., Applied Surface Science 541 (2021): 148612.

Invited Talk

Van der Waals epitaxial growth of 2D materials and heterostructures

Kai Xiao (Center for Nanophase Materials Sciences, Oak Ridge National Laboratory), **Xufan Li** (Oak Ridge National Laboratory), **Yu-Chuan Lin** (Oak Ridge National Laboratory), **Sumner Harris** (Oak Ridge National Laboratory), **Alex Puretzky** (ORNL), **Chris M. Rouleau** (Oak Ridge National laboratory), **Gerd Duscher** (University of Tennessee, Knoxville), **Mina Yoon** (Oak Ridge National laboratory), **David B. Geohegan** (Oak Ridge National laboratory)

Keywords: Fundamentals, Growth; 2D; Novel; CVD; Optical Materials, PLD, Quantum Materials

Van der Waals (vdW) epitaxial growth of 2D materials enables the controlled synthesis of large-area, single crystalline 2D materials and heterostructures with preferred stacking configurations that circumvent the strict lattice-matching requirements in traditional epitaxial growth. In this talk, I will first discuss the vdW epitaxial growth of 2D GaSe crystals on graphene and MoSe2 monolayers by chemical vapor deposition. The DFT calculation and z-contrast STEM imaging reveal that a strong lattice potential corrugation and a small supercell are responsible for the preferred lattice rotation of the 2D materials during growth. Then I will present how to use stepwise pulsed laser heating within a TEM to understand the crystallization and coalescence of 2D material precursors on graphene and MoSe2 monolayers through vdW epitaxy. With in situ TEM, we find that the single crystalline MoSe2 substrate guides the formation of large domain 2D materials both during the crystallization process via direct templating and after crystallization by assisting the coalescence of nanosized domains through nonclassical particle attachment processes including domain rotation and grain boundary migration. The favorable energetics for domain rotation induced by lattice matching with the substrate were understood from first-principles calculations. Therefore, vdW epitaxial growth of 2D materials is a promising approach for the scalable synthesis of large-area, vdW heterostructures for the development of new optical and optoelectronic devices. This work was supported by the U.S. DOE, Office of Science, Materials Sciences and Engineering Division and the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. References 1. Li, X. et al., Van der Waals epitaxial growth of two-dimensional single-crystalline GaSe domains on graphene, ACS Nano, 9, 8078-8088 (2015). 2. Li, X. et al., Two-dimensional GaSe/MoSe2 misfit bilayer heterojunctions by van der Waals epitaxy, Science Advances, 2, e1501882 (2016). 3. Liu, C., et al., Understanding Substrate-Guided Assembly in van der Waals Epitaxy by in Situ Laser Crystallization within a Transmission Electron Microscope, ACS Nano, 15, 8638-8652 (2021). 4. Harris, S., et al., Real-Time Diagnostics of 2D Crystal Transformations by Pulsed Laser Deposition: Controlled Synthesis of Janus WSSe Monolayers and Alloys, ACS nano 17 (3), 2472â€“2486 (2023).

Epitaxial Growth of Transition Metal Dichalcogenide Monolayers by MOCVD for Large Area Device Applications

Andrew Graves (Materials Research Institute, The Pennsylvania State University), **Thomas McKnight** (The Pennsylvania State University), **Nicholas Trainor** (The Pennsylvania State University), **Chen Chen** (The Pennsylvania State University), **Shalini Kumari** (The Pennsylvania State University), **Meghan Leger** (The Pennsylvania State University), **Joan M**. **Redwing** (The Pennsylvania State University)

Keywords: Growth; Low Dimensional, Thin Film, 2D; transition metal dichalcogenide (TMD); CVD; Direct Gap; Electronic Materials

Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS2, WS2 and WSe2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains with the same crystallographic direction. The prospects and challenges associated with the epitaxial growth of wafer-scale TMD monolayers and heterostructures for the development of large area 2D devices will be discussed. Metalorganic chemical vapor deposition (MOCVD) has emerged as an enabling growth technology for TMDs due to its ability to achieve a combination of high growth temperatures (>700Â°C) and large chalcogen overpressures which are needed to obtain stoichiometric epitaxial films. The unique aspects of van der Waals epitaxy of TMDs on sapphire substrates will be presented including the effects of crystallographic orientation of the substrate on nucleation density and domain orientation and the role of surface passivation and steps on domain alignment and defects. Techniques for wafer-scale 2D layer transfer for device integration will be reviewed and applications for wafer-scale TMD monolayers in nanoelectronics, sensing and photonics will be presented.

Growth of BN dielectric layer on GaN by metal organic chemical vapor deposition

Michael Snure (Air Force Research Laboratory), **Eric Blanton** (KBR), **Gordon Grzybouski** (KBR)

Keywords: Growth; 2D; Nitrides; CVD; dielectric; Electronic Materials

Boron nitride has become â€œtheâ€ dielectric passivation layer for two-dimensional (2D) materials and devices. The fully compensated surfaces, weak van der Waals (vdW) bonding between layers, and atomically flat surfaces enable the ability to form atomically abrupt and thin heterostructures with high interface quality. Additionally, its dielectric properties, high surface optical phonon energy and excellent thermal and chemical stability has been extremely successful at preserving and protecting the intrinsic properties of semiconducting 2D materials from the effects of 3D substrates and environment. Similarly, BN offers many of these same advantages to conventional 3D materials and devices including GaN and AlGaN/GaN high electron mobility transistors (HEMTs). GaN metal-insulator-semiconductor (MIS) HEMTs offer improvements over conventional Schottky-HEMTs including higher breakdown, higher efficiency, and normally-off operation. However, MIS-HEMTs using conventional insulators, like SiNx and Al2O3, can suffer from poor interfacial quality and high interface trap densities limiting these improvements. Here we explore the growth and use of BN as a dielectric layer for GaN and AlGaN/GaN HEMT structures grown all by metal organic chemical vapor deposition (MOCVD), which can be done at scale in one continuous process. To achieve high quality BN/GaN interfaces we aim to balance the high temperature requirements for growing BN with GaN decomposition and intermixing between the BN, GaN and AlGaN layers. Using a combination of structural, chemical, and surface characterization techniques we optimize the BN on GaN growth conditions, which is then applied to the growth of BN AlGaN/GaN structures necessary for MIS-HEMTs. Using BN-GaN MIS capacitors we further investigate the interface quality and quantify interface trap densities using C-V and photo-C-V measurements. This work demonstrates the feasibility of using 2D BN as an effective dielectric layer for GaN and AlGaN/GaN MIS-HEMTs.

Invited Talk

Epitaxial Graphene for Sensing Applications

Rachael Myers-Ward (Naval Research Laboratory), **Keith Perkins** (US Naval Research Laboratory), **JongBong Nah** (George Mason University), **Jenifer Hajzus** (US Naval Research Laboratory), **Evgeniya Lock** (US Naval Research Laboratory), **Anthony Boyd** (US Naval Research Laboratory), **Lisa Shriver-Lake**, **Scott Dean** (US Naval Research Laboratory), **Jeffrey Erickson** (US Naval Research Laboratory), **Daniel Zabetakis** (US Naval Research Laboratory), **Joel Golden** (US Naval Research Laboratory), **D. Kurt Gaskill** (UMD), **Daniel Pennachio** (US Naval Research Laboratory), **Scott Trammell** (US Naval Research Laboratory)

Keywords: Characterization, Defects, Growth; 2D; Carbides, graphene; CVD; sensors

Since its discovery, graphene has been recognized for its exceptional physical, electronic and optical properties. While the lack of an energy gap has limited conventional device applications, our research has focused on its chemical sensing abilities. Epitaxial graphene is an attractive material to sense adsorbates, which impact carrier concentration and lead to measureable variations in conductivity. Here, we report on large area, continuous epitaxial graphene grown by the Si sublimation from SiC substrates as the material of choice for sensor development, focusing on underwater and sulfur-bearing vapor sensors. For sensing trace contaminants in seawater, we compared single layer, multilayer and hydrogen-intercalated quasi-freestanding (QFS) bilayer epitaxial graphene (EG) as the working electrode in an electrochemical sensor. Multilayer EG was a stable working electrode for detection of contaminants in seawater. To improve the detection and identification of heavy metals, the graphene was oxidized in an oxygen plasma. Machine learning models were used to identify metals based on the collected library of cyclic square wave voltammetry data for unmodified and oxygen plasma-modified multilayer and hydrogen-intercalated QFS bilayer EG. The results differed according to machine learning model and EG type. Receiver Operating Characteristic (ROC) curves were generated, and the area under the curve (AUC) was used as a metric to compare the performance of the different EG electrodes and machine learning models for heavy metal identification. Hydrogen-intercalated, oxygen-plasma modified QFS bilayer EG was found to have the highest average AUC of 0.998. A chemiresistive sulfur sensor has been demonstrated using single layer EG. Functionalization of the EG is required as graphene is extremely sensitive to molecular adsorption, which changes the conductivity of the material. In order to make the material selective, we functionalize the graphene with metal oxide nanoparticles. We find that this material is highly efficient at sensing sulfur compounds with a detection limit of 0.2 ppm for octanethiol. Further, we observe that different metal oxide chemistries respond differently to different sulfur compounds, thus suggesting a path to specificity.

Invited Talk

Reciprocal Quantum Electrodynamics for Two-Dimensional Materials

Shoufeng Lan (Texas A&M University)

Keywords: Devices, Fundamentals; 2D; Nitrides, Novel; Nonlinear; Optical Materials, Quantum Materials

Cavity quantum electrodynamics (QED) with light confinement in physical space predominantly underpins photon-matter interactions. However, the cavity QED uses only half of the parameter space because position and momentum are canonically conjugate variables governed by the uncertainty principle. The recent realization of photonic bound states in the continuum (BICs) has made possible an exotic scenario in which light confinement is in the other half of the parameter space - momentum space. Here, we will discuss our efforts on artificial intelligence to reduce time and computing resources for designing BICs with extremely narrow spectral features. We then utilized the designed BICs to facilitate the excitation and detection of dark excitons otherwise optically forbidden in 2D materials. We also investigated the topological nature of BICs with the quantized orbital angular momentum in nonlinear high-harmonic generations. We can name the BIC-based QED as reciprocal QED, which we believe could be a general platform for studying photon-matter interactions in nearby materials.

Invited Talk

The synthesis and engineering of two-dimensional Janus quantum layers

Sefaattin (**Seth**) **Tongay** (Arizona State University)

Keywords: Characterization, Defects, Growth; Low Dimensional, 2D; CVD; 2D; Quantum Materials

Named after the two faced Roman God Janus, 2D Janus layers contain two different atomic types on their top and bottom faces. Previous theoretical studies have shown that broken mirror symmetry together with large change transfer across the top and bottom face opens up completely new quantum properties including the Rashba effect, colossal Janus field, dipolar excitons, and Skyrmion formation. Despite the theoretical advances in the field, experimental results are still limited due to limitations in high-quality 2D Janus layer synthesis. In this talk, I will introduce recent discoveries made at Arizona State University towards different types of Janus layers. The growth process relies on Plasma enhanced low-pressure chemical vapor deposition (PE-LPCVD). With this all-room temperature technique, our team can synthesize different Janus layers, their vertical/lateral heterojunctions, and Janus nanoscrolls. Further studies from our team will introduce on-demand fabrication of 2D Janus layers with unique in-situ growth capabilities that allows us to collect spectroscopy data during the course of Janus material growth. Results are presented along with microscopy, spectroscopy, high-pressure studies, and electronic transport datasets for a complete understanding of these systems1-5.

Invited Talk

Towards novel morphologies of 2D materials: intercalation and twists

Jie Yao (UC Berkeley)

Keywords: Characterization, Growth; Low Dimensional, Group IV chalcogenides, 2D; CVD, Ferromagnetic, PVT, Solution Growth, VPE; Ferroelectric, Oxides, Twisted Crystal; Energy Materials, Optical Materials, Quantum Materials

I will first introduce our recent work on the preparation of monolayer crystalline oxide using graphene-based templates. By intercalating metal ions into the van der Waals gaps of graphene oxide layers, we are able to generate metal oxide monolayers and bilayers. The graphene oxide layers can be removed via a burning process. Such polycrystalline binary oxide layers can be placed on different substrates. We also achieved doping of such layers with a wide range of dopant concentrations. In particular, the doping of ZnO monolayers/bilayers with cobalt atoms allows us to achieve 2D ferromagnetism with controllable magnetic responses. Another direction I would discuss is the growth of 2D layers with twisted stacking. By introducing screw dislocations to the vapor phase deposition of a typical 2D material GeS, we successfully achieved spiral growth of the 2D materials. Most interestingly, there is a twist between the adjacent layers. Such twists are so-call Eshelby twists and can be tuned during the growth process, giving us a great opportunity in exploring the twist degree of freedom. I will also briefly discuss some of the intriguing properties of such twisted crystals.

Invited Talk

Layered topological semimetals for novel high-performance electronics and THz optoelectronics

Jun Xiao (University of Wisconsin Madison)

Keywords: Characterization, Devices, Fundamentals; Low Dimensional, 2D; Novel; Flux Growth; Ferroelectric; Optical Materials, Quantum Materials

The emergent atomically thin layered materials enable the unique control of new phases of matter for high-performance electronics and optoelectronics. In this talk, I will report how the novel quantum properties of layered topological semimetals can substantially influence their electron transport and optical responses. In particular, I will introduce the manipulation of quantum geometrical properties in a ferroelectric topological semimetal (WTe2) via certain stacking order transition [1]. With such control and various characterization means, we observed substantial modulation in optical and electrical responses associated the unique stacking orders in such exotic ferroelectric semimetal. Further nonlinear Hall transport measurements show the observed transitions are locked with the variation of topological and geometrical property. Our findings lead to a new low-energy-cost, electrically controlled topological memory in the atomically thin limit. Along this line, I will show our recent demonstration on high-performance THz sensing devices based on those new discovered effects. References: [1] J. Xiao et al., Berry curvature memory through electrically driven stacking transitions, Nature Physics 16, 1028.

Invited Talk

Novel plasmonic effects in 2D materials

Tony Low (University of Minnesota)

Keywords: Devices, Fundamentals; 2D; Optical Materials

Plasmons in 2D materials are interesting as they reside in the highly sought after mid-infrared spectrum, which finds applications in gas and biomolecule sensing and free space communications. These plasmons are electromagnetic modes confined to the surface of the 2D materials, and they provide a means of shrinking the free space wavelength of mid-infrared light by two orders of magnitude, thus enhancing light-matter interactions and more efficient focusing of electromagnetic energy for various applications. In this talk, I hope to impress upon you that the wide range of electronic properties in 2D materials opens the door to the engineering of a plethora of novel mid-infrared plasmonic effects which has to-date been inaccessible in conventional plasmonic materials like bulk noble metals. This includes slow plasmons in bilayer graphene, chiral plasmons in twisted bilayer graphene, hyperbolic plasmons in anisotropic materials, Berry plasmons in massive Dirac like materials, plasmons immune to Landau damping in finite electronic width materials, and current driven amplified plasmons in WTe_2. I will also review related experiments where these effects have recently been reported.

Invited Talk

2D Materials Electronic and Optoelectronic Device Applications

Sina Najmaei (US Army Research Lab)

Keywords: Devices, Growth; 2D; CVD, Flux Growth, MBE, ALD; Ferroelectric, Excitonics; Optical Materials, Electronic Materials

2D materials have for many years been at the center of attention in the semiconducting research communities that have a strong focus on advancing the computing and sensing capabilities of future technologies. In this talk I will examine the unique role van der Waals materials can play in some of the future technologies by focusing on examples of promising back-end of line integrable 2D neuromorphic computing and photodetectors devices. I will focus on the distinctive basic material processing and device integration challenges that these materials possess and demonstrate solutions that we have been exploring in our team to build a roadmap for incorporation of these materials in these game changing applications.

Invited Talk

Growth and Emerging Functionality of van der Waals Crystals and Heterostructures

Eli Sutter (University of Nebraska-Lincoln), **Peter Sutter** (University of Nebraska-Lincoln)

Keywords: Low Dimensional; Chalcogenides; PVT; Ferroelectric, Twisted Crystal; Energy Materials, Optical Materials

Van der Waals nanowires are a new class of materials in which layered crystals â€“ consisting of covalently bonded sheets held together by weaker van der Waals forces â€“ are shaped into 1D nanostructures. With their highly anisotropic crystal structure, van der Waals nanowires incorporate unique degrees of freedom not found in conventional 3D crystals, such as a variable layer orientation, ubiquitous crystal defects, and novel types of heterostructures. Due to this structural diversity, seemingly innocuous changes to the growth process, e.g., by alloying, can have drastic consequences on the resulting nanostructures. Here, we discuss the growth of 1D nanostructures of GeS1-xSex, a system of layered monochalcogenide alloys with tunable bandgap and other promising functionality, combining the concepts of vapor-liquid-solid (VLS) growth and van der Waals epitaxy. The pure endpoint materials, GeS and GeSe, adopt entirely different morphologies. GeS nanowires crystallize with layering along the wire axis [1] and have a strong propensity for forming axial screw dislocations, which give rise to a chiral structure with tunable electronic properties due to an interlayer twist moirÃ© and carrier confinement [2-4]. GeSe, on the other hand, grows as large nanoribbons with layering parallel to the symmetry axis [5]. VLS growth of GeS1-xSex alloys demonstrates that the morphology switch from ribbons to wires occurs already at S contents of a few percent. The resulting GeS1-xSex nanowires exhibit surprising characteristics involving extended defects. The spontaneous incorporation of single-layer stacking faults in the otherwise centrosymmetric stacking sequence breaks mirror symmetry, turning the wires into ferroelectrics where each of the inserted layers carries a switchable polarization [6]. GeS1-xSex alloys with higher S content show a tunable bandgap that varies linearly with composition, and which can further be extended to higher energies by carrier confinement. At high S content, finally, GeS1-xSex components with different bandgaps are self-assembled into mixed-dimensional GeS1-xSex van der Waals heterostructures consisting of 2D/layered plates suspended along 1D nanowires [7]. Here, selective transport through the VLS catalyst gives rise to different alloy compositions of wires and plates, producing bandgap differences that are further augmented by quantum confinement in the wires. Our combined results illustrate the surprising range of structures, morphologies, and functional properties that can be realized via VLS growth of van der Waals nanostructures. 1. E. Sutter and P. Sutter, ASC Appl. Nano Mater. 1, 1042 (2018). 3. P. Sutter, S. Wimer and E. Sutter, Nature 570, 354 (2019). 2. E. Sutter and P. Sutter, Small 17, 2104784 (2021). 4. P. Sutter, J.C. Idrobo, and E. Sutter, Adv. Funct. Mater. 31, 2006421 (2021). 5. E. Sutter, J. S. French, and P. Sutter, Nanoscale 14, 6195 (2022). 6. E. Sutter, H. P. Komsa, A. A. Puretzky, R. R. Unocic, and P. Sutter, ACS Nano 16, 21199 (2022). 7. E. Sutter, J. S. French, and P. Sutter, Chem. Mater. 34, 8868 (2022).

Invited Talk

Heterostructuring by Mechanochemical Reshuffling of Layered 2D - Metal Chalcogenides.

Viktor Balema (ProChem Inc.)

Keywords: Growth, synthesis; Low Dimensional, Heterostructures; Novel, Chalcogenides; Mechanochemical; UWBG/WBG Semiconductor; Energy Materials, Quantum Materials

Heterostructures with incommensurate arrangements of well-defined building blocks are created using an unconventional synthetic approach comprising of mechanically facilitated â€œreshufflingâ€ of layered 2D â€“ transition metal dichalcogenides [1,2], and non-layered rare-earth metal monochalcogenides [2]. The discovered solid-state transformations are directed by quantum interaction between chemically and structurally dissimilar solids toward atomic-scale ordering. In the case of layered MoS_2 and HfS_2 [1], heterostructuring is energetically favorable over the formation of homogeneous nigh entropy dichalcogenides [3]. Density-functional theory calculations validate experimental results. The obtained hetero assemblies demonstrate diverse electron transport behaviors, varying from metallic conductivity to indirect band gap semiconductivity, and superconductivity in some misfit heterostructures [1-4] References [1] Hlova IZ et al. Incommensurate transition-metal dichalcogenides via mechanochemical reshuffling of binary precursors. Nanoscale Adv. 2021; 3: 4065 â€“ 4071. [2] Hlova IZ et al. Multi-principal element transition metal dichalcogenides via reactive fusion of 3D-heterostructures Chem. Commun. 2018; 54: 12574 â€“ 12577. [3] Dolotko O. et al. Unprecedented generation of 3D heterostructures by mechanochemical disassembly and re-ordering of incommensurate metal chalcogenides. Nature Commun. 2020; 11: 3005. [4] Sreedhara MB et al. Nanotubes from the Misfit Layered Compound $(SmS)_{1.19}TaS_2$: Atomic Structure, Charge Transfer, and Electrical Properties. Chem. Mater. 2022; 34: 1838 â€“ 1853.

Invited Talk

Spintronic Quantum Phase Transition in a Graphene/Pb0.24Sn0.76Te Topological Heterostructure with Giant Rashba Spin Texture

Jennifer DeMell (Laboratory for Physical Sciences), **Gregory M**. **Stephen** (Laboratory for Physical Sciences), **Ivan Naumov** (Howard University), **Nicholas A**. **Blumenschein** (Laboratory for Physical Sciences), **Jeremy T**. **Robinson** (NRL), **Patrick J**. **Taylor** (ARL), **Pratibha Dev** (Howard University), **Aubrey T**. **Hanbicki** (Laboratory for Physical Sciences), **Adam L**. **Friedman** (Laboratory for Physical Sciences)

Keywords: Devices; Thin Film, 2D; Novel; CVD, MBE; Topological; Spintronics, Quantum Materials

Quantum phase transitions can provide a low-power switching mode for novel electronic devices for future computing platforms. Heterostructures of novel materials such as topological insulators and two-dimensional (2D) materials possess several unique characteristics, including spin momentum locking, high spin-orbit coupling, and susceptibility to proximity effects. In a previous work we identified the carrier mobility of a Pb0.24Sn0.76Te/graphene heterostructure to be nearly 100% greater than the mobility of either constituent Pb0.24Sn0.76Te or graphene. In this work, we fabricate and measure non-local spin valves on a Pb0.24Sn0.76Te/graphene heterostructure and calculate spin lifetimes on the order of 2 ns with spin polarization efficiencies up to 10%. We found a spin-split two-dimensional electron gas (2DEG) forms at the 2D-material/topological-insulator interface and observe a quantum phase change near 50 K. Below the transition temperature, the non-local resistance exhibits metallic behavior as the 2DEG dominates the device operation and in the high-temperature regime, we observe semiconducting behavior where the classical Rashba effect dominates. This spin valve is robust and continued to operate after a significant time out of vacuum.

Invited Talk

Structure-optimized phosphorene for super-stable potassium storage

Apparao Rao (Clemson University), **Jie Guan** (Hunan University), **Bingan Lu** (Hunan University)

Keywords: Devices; Low Dimensional; Phosphorene; CVD; Electrochemistry; Sustainable Materials

Due to its unique two-dimensional structure and high theoretical capacity, few-layer phosphorene is a promising anode material in potassium ion batteries (PIBs). However, phosphorene suffers from poor electronic properties and large volume expansion during the potassiation/depotassiation process. Here, we report a facile synthesis method for a high-performance phosphorene-carbon nanotubes-polyaniline ((P-CNTs)/PANI) composite that effectively improves electronic properties and alleviates the volume change leading to super-stable high-performance potassium storage. The significance of (P-CNTs)/PANI structural design lies in that CNTs serve as electron transport channels and improve the conductivity of phosphorene, while the PANI coating alleviates the structural degradation caused by volume expansion of phosphorene. Structure-optimized (P-CNTs)/PANI anodes showed (i) a high reversible capacity of 642.7 mAh g-1 at 50 mA g-1 and a maximum reversible capacity of 417.6 mAh g-1 at 500 mA g-1 during stable cycling, (ii) a super-stable electrochemical performance with a capacity retention rate of 94% when the stable cycling exceeded 500 times, while the average capacity decay rate per cycle was as low as 0.012%, and (iii) an excellent rate performance of 212.6 mAh g-1 at 1000 mA g-1. Specifically, the influence of PANI coating on the structure and properties of composites is elucidated. The results show that (P-CNTs)/PANI has a more stable structure and superior performance than P-CNTs. This study provides a new structural design for developing phosphorene-based anodes with an excellent combination of capacity and stability.

Invited Talk

Electrical Transport and Phase Modulation in Two-Dimensional Topological Superconductors

Jifa Tian (University of Wyoming)

Keywords: Characterization; Low Dimensional, superconductivity, 2D; Novel; CVT; Quantum Materials

Exploration of the exotic properties inherent in topological quantum materials has surged to the forefront of condensed matter physics research, driven by their potential applications in future fault-tolerant quantum computing. Topological superconductors, in particular, hold promise as hosts for Majorana fermions â€" unique particles that serve as their own antiparticles. The non-Abelian statistics featured by Majorana fermions make them appealing for the creation of topological quantum bits (qubits), which offer superior robustness against environmental noise in comparison to conventional qubits. In this talk, I will present our research into the properties and potential applications of 2M phase tungsten disulfide (2M-WS2), a recently identified candidate for a two-dimensional (2D) topological superconductor. The first part of the discussion will revolve around our investigation into the intrinsic properties of 2M-WS2, including the growth of bulk crystals and the thickness-dependent electrical transport properties. In the second half, I will delve into our findings on the superconducting-to-semiconducting phase transition in atomically thin 2M-WS2 layers. Our research holds the potential to pioneer a new method for inducing topological phase-change in 2D topological superconductors. The implications of this could significantly influence the development of atomically scaled planar topological Josephson junctions for topological qubits.

Invited Talk

Synthesis of Transition Metal Dichalcogenides on oxide surfaces

Stephen McDonnell (The University of Virginia), **Maria Gabriela Sales** (The University of Virginia), **Clayton Rogers** (The University of Virginia), **Abir Hasan** (The University of Virginia), **Alex L Mazzoni** (Intel Corporation), **Christopher Jezewski** (Intel Corporation), **Carl H**. **Naylor** (Army Research Laboratory), **Sina Najmaei** (Army Research Laboratory), **Wendy L Sarney** (The University of Virginia), **Nikhil Shukla**

Keywords: Growth; 2D; Novel; MBE; semiconductor and semi-metal; nanoelectronic

2D materials, which include graphene, hexagonal boron nitride, and a plethora of transition metal dichalcogenide (TMDC) combinations, have electronic structures exhibiting metallic, semiconducting, and insulating properties. This promises devices with scalability to the atomic limit combined with tunable bandgaps that can be direct or indirect and defect free interfaces. Presented will be our summary of our recent work investigating the deposition of TMDCs on ferroelectric and linear dielectric substrates. We will show how deposition conditions can impact not just the grown material, but also the substrate. During growths of WSe2 on hafnium zirconium oxide, chalcogens can diffuse into oxide substrates resulting in Fermi level shifts which we speculate is due to oxygen vacancy passivation. This will be important for integration of these materials into nanoelectronics device architectures. In separate work, we investigate the properties of NbSe2 deposited on SiO2. We report on the electronic properties, specifically resistivity, and their dependence on growth conditions and nanoelectronic device fabrication process.

Invited Talk

New Functional Heterostructures Through Low-Temperature Growth of van der Waals Materials

Christopher Hinkle (University of Notre Dame)

Keywords: Characterization, Devices, Growth; Ferromagnetic, 2D; Novel; MBE

The low-temperature growth of van der Waals materials opens the door for new integration schemes for nanoelectronic, optoelectronic, and spintronic devices. Functional heterostructures of different transition metal dichalcogenides (TMDs), multiferroic oxides with magnetically doped TMDs, and 2D/3D semiconductor stacks will all be discussed focusing on their synthesis, interface quality, and the devices they enable.

Growth and Emerging Functionality of van der Waals Crystals and Heterostructures

Peter Sutter (University of Nebraska-Lincoln), **Eli Sutter** (University of Nebraska-Lincoln)

Keywords: Characterization, Growth; 2D; Chalcogenides; PVT; Ferroelectric, Optoelectronics and Photonics

An ever-growing family of atomically thin (2D) crystals has attracted sustained research interest for more than a decade. In contrast, few-layer and multilayer van der Waals crystals and heterostructures have remained far less explored. Layered crystals present unique structural degrees of freedom, for example different layer stacking arrangements, interlayer twist, and the formation of novel heterostructure architectures with diverse interface geometries. The development of crystal growth approaches that provide control over these characteristics can unlock multifaceted functionality such as interfacial management of light-matter interactions or ferroelectricity, in support of future technologies relying on energy and information flows at the nanoscale. Here, we discuss recent progress in addressing the synthesis challenges of van der Waals materials and in probing their functional properties at the relevant scales. We focus on group IVA (Ge, Sn) chalcogenides, an emerging class of layered semiconductors with multiple stable polymorphs that harbor promising functionality. We demonstrate bottom-up approaches for realizing non-equilibrium layer stacking, which can break the innate mirror symmetry of these crystals and turn them into ferroelectrics [1,2]. Suitable growth protocols can yield twisted layer stacks and â€˜twist superlatticesâ€™ [3]. Group IVA chalcogenides also lend themselves exceptionally well to the creation of heterostructures. Architectures such as multilayer lateral heterostructures [4,5] and axially twisted nanoribbons [6], probed by nanometer-scale cathodoluminescence spectroscopy, display carrier transfer and -separation at interfaces as well as propagating nanophotonic hybrid light-matter modes. Our results point to a rich set of structures and functionalities that can be accessed through the controlled synthesis of van der Waals crystals. [1] P. Sutter, H.P. Komsa, H. Lu, A. Gruverman, E. Sutter, Nano Today 37, 101082 (2021). [2] E. Sutter, H.-P. Komsa, A.A. Puretzky, R.R. Unocic, P. Sutter, ACS Nano 16, 21199 (2022). [3] P. Sutter, R. Ibragimova, H.-P. Komsa, B.A. Parkinson, E. Sutter, Nature Communications 10, 5528 (2019). [4] E. Sutter, J. Wang, P. Sutter, ACS Nano 14, 12248 (2020). [5] E. Sutter, R.R. Unocic, J.-C. Idrobo, P. Sutter, Advanced Science 9, 2103830 (2022). [6] P. Sutter, L. Khosravi Khorashad, C. Argyropoulos, E. Sutter, Advanced Materials 33, 2006649 (2021).

Career Panel Event for Students

Kevin Schulte (AACG)

Keywords:

The AACG will hold a panel event for students and postdoctoral researchers interested in learning about various career paths in crystal growth. The event will feature speakers from academia, industry, and national laboratories who will describe what it is like to work in each of these organizations, and the path they took to get where they are today. The event will begin with short presentations from each of the panel, followed by an open discussion in which the panel will answer questions posed by the audience. Pizza and refreshments will be provided.

The event takes place Tuesday August 15, 6:30-8:00 PM in the Aster room.

Poster

Development of Ce doped LiGdCl4/LiCl eutectic as a high concentration 6Li contening thermal neutron scintillator

Kei Kamada (Tohoku univ.)

Keywords: Growth; Bulk; chloride; Melt Growth; Scintillator; Scintillator Materials

Thermal neutron detection has a wide range of ap-plications, including medicine, nondestructive testing, structural analysis, astronomical observation, moisture imaging in plants, and resource exploration. In an envi-ronment using a neutron detector, radiation in the form of Î³-rays exists in addition to neutrons, making it necessary to efficiently distinguish neutron rays. Therefore, a scin-tillator with high sensitivity to neutron rays and low sen-sitivity to Î³-rays is required. Thermal neutron detectors are composed of gas, liquid, and solid scintillators con-taining 3He, 6Li, 10B, and 157Gd, which offer a large neu-tron capture cross-section. In recent years, scintilla-tion detectors using inorganic solid scintillators contain-ing 6Li have been increasingly employed owing to their ease of handling and radiation resistivity. In these detectors, the scintillators absorb the Î±-rays generated by the 6Li (n, Î±) 3H reaction and convert them into visible light. In this study, a Ce-doped LiGdCl4/LiCl eutectic with a high 6Li concentration was developed as a novel thermal neutron scintillator. Ce-doped LiGdCl4 was selected as the scintillator phase. Ce doped LiGdCl4 not only contains Li, but also has a fast decay component of less than 50 ns due to the Ce3+ 4f5d transition and low density of 3.60 g/cm3. The Ce-doped LiGdCl4/LiCl eutectic was grown using the vertical Bridgman method in a sealed quartz ampoule. The eutectic ex-hibited a lamellar eutectic structure and showed slight optical transparency. The emissions at 370 nm were attributed to the Ce3+ 4f-5d transition. The light yield under 252Cf thermal neutron was estimated to be 2,600 photons/neutron. The scintillation decay time was 46 ns.

Invited Talk

Intrinsic Tl-based Halide Scintillators for Particle Detectors

Rastgo Hawrami (Xtallized Intelligence, Inc.)

Keywords: Growth; Melt Growth; Scintillator; Scintillator Materials

Recently high detection efficiency Tl-based halide scintillation crystals have attracted good attention from worldwide scintillator researchers. In this paper, we will present material preparation, growth, and basic scintillator performance of Tlbased intrinsic, non-hygroscopic ternary compounds TlA2X5 and TlAX3, where A = Sr, Mg, Ca, Cu, Ce, or Ba, and X = Cl, Br, I or mixed halides. Crystal structure verification by x-ray diffraction, phase study, and compound analysis are performed. Crystal growth, started with material purification and synthesis, initial small diameter crystal growth, followed by a successful scale up of well-performing one-inch bulk single, crack-free, transparent, intrinsic Tlbased TlA2X5 and TlAX3 scintillators, as well as 137Cs spectra, decay time and nonproportionality data, will be presented.

First Bridgman growth of RbSrI3:Eu scintillator for high energy X-ray radiography

Kimberly Pestovich (University of Tennessee), **Luis Stand** (University of Tennessee), **Charles Melcher** (University of Tennessee), **Edgar van Loef** (Radiation Monitoring Devices, Inc.), **Lakshmi Pandian** (Radiation Monitoring Devices, Inc.), **Mariya Zhuravleva** (University of Tennessee)

Keywords: Characterization, Growth; Bulk; halides; Melt Growth; Scintillator; Scintillator Materials

To secure the global supply chain, high energy X-ray radiography is used to screen cargo crossing borders. Scintillators currently used in these applications have limitations in properties that can hinder imaging capabilities or are cost restrictive. To overcome these limitations, research into novel inorganic perovskites supports efforts to identify high light yield, low afterglow, radiation hard scintillators. In this work, a new promising perovskite scintillator RbSrI3:Eu was grown from the melt for the first time. RbSrI3 crystallizes in a Cmcm space group with a density of 4.1 g/cc and effective atomic number of 49. Differential Scanning Calorimetry was used to determine melting point and revealed incongruent melt behavior. High temperature X-ray Diffraction confirmed the absence of structural phase transitions and showed mild anisotropy of the coefficients of thermal expansion. Crystals were grown via the Bridgman method in a Ã˜7 mm size with different dopant concentrations to assess scintillation properties, resulting in highest light yield of 84,000 ph/MeV. Additionally, radiation hardness for dose points of 100 krad and 1 Mrad was investigated with a Co-60 source. Other crystals were grown in Ã˜12 and Ã˜22 mm sizes to assess potential for scale up. Since the crystals are sensitive to moisture, sealing of crystals in protective packaging is under consideration. Overall, it was found that RbSrI3:Eu has promising properties for high energy X-ray radiography, like high light yield and relatively low afterglow.

Thermophysical Property Measurements of Indium Iodide Crystals

Martin Volz (NASA Marshall Space Flight Center), **Arne Croell** (University of Huntsville in Alabama), **Vladimir Riabov** (Illinois Institute of Technology), **Aleksander Ostrogorsky** (Illinois Institute of Technology)

Keywords: Characterization; Bulk; III-VII; Melt Growth, PVT; UWBG/WBG Semiconductor; Optical Materials

InI single crystals are a promising room temperature detector material for X-rays and Î³-rays. To improve crystal growth of the material by simulations, knowledge of thermophysical properties is essential, and since InI is orthorhombic, the anisotropy has to be taken into account. The temperature dependence of several thermophysical properties have been measured for InI, including the anisotropic thermal expansion, specific heat, and the thermal diffusivity in the b direction. The anisotropic thermal expansion coefficients, determined by X-ray diffraction, were Î±11=1.03Â·10-5 K-1, Î±22= 3.77Â·10-5 K-1, and Î±33 = 6.26Â·10-5 K-1. The specific heat, measured by DSC, was 0.226 J g-1 K-1 at 335K, with a temperature dependence of 9.582 Â·10-5 J g-1 K-2. In the course of the X-ray diffraction and DSC measurements, it was shown that supposed phase changes, reported in older literature, are actually not phase changes but oxidation effects. The thermal diffusivity in the b direction, measured by the Xenon Flash method, was 0.288Â·10-6 m2s-1 at RT, decreasing to 0.253Â·10-6 m2 s-1 at 450K. In addition, the volume increase upon melting and the thermal expansion of the melt have been determined.

Using In-situ Sublimation Methods in the Growth of Halide Perovskite Single Crystal Semiconductors

Peng Wang (Department of Chemistry, Queenâ€™s University), **David Kunar** (Queen's University), **Matthew Webster** (Department of Chemistry, Queen's University), **Michael Lewis** (Queen's University)

Keywords: Growth, Technology/Equipment; Bulk; Novel; Melt Growth, PVT; UWBG/WBG Semiconductor; Optical Materials

Room-temperature semiconducting radiation detectors have been applied in many different fields, such as medical imaging, national security, and scientific research. Functioning radiation detectors must exhibit excellent optoelectronic properties including a large carrier-mobility lifetime and a high photo sensitivity. These optoelectronic properties depend strongly on materials the purity and crystalline. As a result, the state-of-the-art radiation detection materials are obtained via multi-step purification and crystal growth processes. These isolated purification, synthesis, and crystal growth protocols are vulnerable to the introduction of extrinsic impurities. In addition, the separated thermal cycles (i.e., heating/cooling time) result in a relatively low production efficiency. In this work, we report in-situ sublimation methods combining the purification and the crystal growth into a continuous process in a single reaction vessel. Several semiconducting radiation detector materials were produced by adapting in-situ sublimation to the chemistry of each compound. The single crystals were cut, polished, and fabricated in to detectors for electrical and photocurrent response tests. A few compounds demonstrated clear spectroscopy responses to high energy ionizing radiation.

Invited Talk

The Luminescence of Aluminate Spinels: The Role of Defects and Impurities

Luiz Jacobsohn (Clemson University), **Robin L. Conner** (Clemson University)

Keywords: Characterization; Bulk; Oxides; Co-precipitation; Dosimeter; Dosimetry

Spinels present large compositional diversity and property tunability and thus are of interest to many technology fields. The cubic structure and broad optical transparency associated with a large band gap of the Mg and Zn aluminate spinels make these materials particularly attractive for optical applications. Also, the capacity of accommodating relatively large amounts of anti-site defects make them good candidates for applications involving radiation damage. MgAl2O4 and ZnAl2O4 in a diversity of forms, from powders prepared by the co-precipitation method and calcined at 900 oC for 2 hrs. in air to natural crystals and artificial crystals grown by the Czochralski method, were investigated. Structural characterization was executed by X-ray diffraction and Raman spectroscopy. Radioluminescence (RL) under X-ray excitation from room temperature to 400 oC was recorded towards the identification of all luminescence centers present in the different materials. RL measurements revealed that both spinels presented a broad band peaked at ~400 nm attributed to antisites and other defects, and bands attributed to Cr3+, Mn4+ and Mn2+ impurities. Thermoluminescence (TL) spectroscopy measurements up to 400 oC were executed towards the identification of the recombination centers involved in the TL process, with the glow curves presenting several overlapping bands. TL spectroscopy measurements showed TL signal to be originated mostly from Cr3+ impurities. The stability of TL signal storage (fading) was also evaluated. This material is based upon work supported by the National Science Foundation under Grant No. 1653016, and by a NASA South Carolina Space REAP Grant.

Invited Talk

Recent developments in Scintillator Co-doping at Luxium Solutions

Peter Menge (Luxium Solutions), **Vladimir Ouspenski** (Saint-Gobain Research Paris), **Fang Meng** (Luxium Solutions), **John Frank** (Luxium Solutions)

Keywords: Defects; Bulk; Halides; Melt Growth; Scintillator; Scintillator Materials

Recent years have brought much interest to the area of co-doping of crystal scintillators to improve specific properties. Although many crystal scintillators contain dopants necessary for optical activation, â€œco-dopantsâ€□ refer to strategic impurities intentionally grown in the crystal (usually at levels far less than the activators), and they play a more subtle role than the activator in the scintillation process. This field of endeavor is also called defect- or band gap-engineering and has brought new life to mature, stalwart scintillators such as NaI(Tl), CsI(Tl) and LaBr3(Ce). Co-doping has been used for improving light output, energy resolution, and speed of the light pulse. It has been used to augment the emission spectrum, pulse shape discrimination, and sensitivity to specific radiation particles. A surprising discovery made over the last several years is that often only very low concentrations of co-dopant (0.1 â€“ 20 ppm) can bring about significant enhancements to scintillation properties and applications such as radioisotope identification and industrial/medical imaging. Low concentration co-doping is advantageous for crystal growth because very little need be changed to the already industrialized growth processes of the mature scintillators, since very little lattice distortion occurs in the crystal matrix. This report will detail recent Luxium Solutions discoveries in the areas of low concentration co-doping. Specifically, the improvements to LaBr3(Ce) co-doped with group I and II elements, and CsI(Tl) co-doped with group VB elements will be discussed along with proposed physical mechanisms for the measured improvements. Future directions in co-doping will also be presented, particularly regarding multiple co-dopants and combining deep and shallow charge carrier trapping.

Discovery and Scale Up of New Ultrafast Chloride Scintillators

Daniel Rutstrom (University of Tennessee), **Luis Stand** (University of Tennessee), **Maciej Kapusta** (Siemens Medical Solutions), **Charles L. Melcher** (University of Tennessee), **Mariya Zhuravleva** (University of Tennessee)

Keywords: Characterization, Growth; Bulk; halides; Melt Growth; Scintillator; Scintillator Materials

Recently, we have demonstrated the potential of novel single crystal scintillators Cs3ZnCl5 and Cs2ZnCl4, which offer ultrafast decay times (0.8-1.7 ns) and relatively high core valence luminescence (CVL) light yields (1,000-2,000 ph/MeV). These new materials provide several advantages over state-of-the-art BaF2, a commercially available inorganic scintillator that has received attention for use in medical imaging (using the heterostructure or metascintillator concept) and high energy physics (HEP) experiments due to its ultrafast timing capabilities and moderate density. So far, Bridgman growth of Cs3ZnCl5 and Cs2ZnCl4 crystals has been accomplished for sizes up to 22 mm in diameter; however, larger-volume crystals are often more practical or even necessary to improve detection efficiency. In the current work, we show that nearly crack-free Cs2ZnCl4 crystals can be grown 38 mm (1.5â€□) in diameter. To assess the extent that thermal expansion may contribute to cracking, coefficients of thermal expansion (CTE) are determined from temperature dependent X-ray diffraction (XRD) measurements (from 25 Â°C to 350 Â°C). Additionally, new compositions with ultrafast CVL are explored, and it is found that Zn-doping can improve the light yield of CsMgCl3 (29.6% increase for 5 mol% Zn) and Cs2MgCl4 (10.9% increase for 5 mol% Zn). Coincidence time resolution (CTR) is measured for various crystals, and the best result is obtained with CsMgCl3:Zn 5% (CTR = 98 ps FWHM). The results of this work show that Cs2ZnCl4 is not only promising from a performance perspective, but also its ability to be fabricated as large-volume single crystals. We also demonstrate that compositional engineering may allow for fine-tuning of the scintillation and timing properties of various ultrafast CVL crystals.

Invited Talk

Cd1-x-yMgxZnyTe, a New Alternative High-Performance Radiation Detector Material

Sudhir Trivedi (Brimrose Technology Corporation), **Sue Kutcher** (Brimrose Technology Corporation), **Corey Rosemier** (Brimrose Technology Corporation), **Siva Ram Swaminathan** (Brimrose Technology Corporation), **Henry Chen** (Henry Chen Consulting LLC)

Keywords: Detector Materials; Bulk; II-VI; Melt Growth; UWBG/WBG Semiconductor; Semiconductor Detectors

A new, high performance and low cost solid-state radiation detector material, Cd1-x-yMgxZnyTe (x=0.05-1, y=0.02-0.04) (CMZT) has been developed by Brimrose Technology Corp, as an alternative to current COTS room temperature semiconductor detectors such as CZT. CMZT is a practical, achievable radiation detector material, unlike other alternative materials proposed over the years such as TlBr, CdMnTe, CdZnTeSe, and more recently CsPbBr3 that share similar material issues: difficult in device fabrication, detector instability or poor crystallinity and homogeneity resulting in poor detector performance and moreover high cost. The new CMZT has been grown by the conventional Bridgman method with high yield and detector performance approaching that of CZT at room temperature without signal correction. The crystal growth and detector performance of this material will be presented and discussed.

Physical Properties of CsPbBr3 Crystal and Bridgman Crystal Growth

Duck Young Chung (Argonne National Laboratory), **Indra Pandey** (Argonne National Laboratory, Northwestern University), **Mustafa Unal** (Argonne National Laboratory), **Mercouri Kanatzidis** (Argonne National Laboratory, Northwestern University)

Keywords: Characterization, Defects, Devices, Growth; Bulk; Perovskite; Flux Growth, Melt Growth, Solution Growth; Narrow Semiconductor, UWBG/WBG Semiconductor; semiconductor detector materials

The perovskite CsPbBr3 is a new generation semiconductor in the field of X-ray and ï□§-ray detection. The fundamental physical properties of CsPbBr3 well meet the requirements for high energy detector applications, with direct band gap (orange color, 2.25 eV), high density (4.85 g/cm3), attenuation coefficient comparable to CZT, and high resistivity (109-1010 ï□—âˆ™cm) and carrier mobility-lifetime product (10-4 cm2/V). We developed a new chemical process for inexpensive material production with an excellent purity (>5N) and quantitative (>95%) yield. Large crystals of CsPbBr3 grown by the Bridgman method show high transparency (85% transmission in FT-IR spectroscopy) and well resolved characteristic peaks in ï□§-ray spectroscopy with 241Am, 57Co, and 137Cs and high flux X-rays as radiation sources. The energy resolution of the planar detector has reached the value close to 1% from the 137Cs ï□§-ray irradiation. The major challenge currently lying in practical detector applications is the crystal defects including domain and twin boundaries and the defect states present in the material, both of which should be minimized. This presentation will give an overview of the process of crystal growth and optimization process that can mitigate these issues with crystal quality and detector performance of CsPbBr3.

Crystal Growth, Density Functional Theory, and Scintillation Properties of TlSr2Cl5 and Tl2Sr2Br5

Edgar van Loef (Radiation Monitoring Devices, Inc.), **Lakshmi Soundara Pandian** (Radiation Monitoring Devices, Inc.), **Guido Ciampi** (Radiation Monitoring Devices, Inc.), **Luis Stand** (University of Tennessee, Knoxville), **Mariya Zhuravleva** (University of Tennessee, Knoxville), **Charles Melcher** (University of Tennessee)

Keywords: Characterization, Fundamentals, Growth, Modeling; Halides; Melt Growth; Scintillator; Scintillator Materials

In recent years, there has been a tremendous surge in the discovery of high-density halide scintillators, driven in part by government funded research of substituting low-Z elements in ordinary halide scintillators with thallium, lead, or bismuth ions. Examples of these include Tl2LaCl5, Tl2LaBr5, Tl2LiYCl6, TlSr2Cl5, TlSr2Br5, TlSr2I5, TlCaCl3, TlCaBr3, and TlCaI3. As a follow up on our previous research into TlSr2I5 [11], in this paper we report on the crystal growth, density functional theory (DFT) and scintillation properties of TlSr2Cl5 and TlSr2Br5. Small diameter crystals were grown by the Vertical Bridgman method in single- and dual-zone furnaces. X-ray diffraction measurements show that TlSr2Cl5 and TlSr2Br5 have a monoclinic crystal structure with space group P21/c. TlSr2Cl5 and TlSr2Br5 have a density of 3.60 g/cm3 and 5.03 g/cm3, respectively. The effective Z of TlSr2Cl5 and TlSr2Br5 is 63.7 and 58.6, respectively. Radioluminescence spectra of TlSr2Cl5 and TlSr2Br5 feature a broad emission band peaking at 450 and 440 nm, respectively. The light yield of TlSr2Cl5 and TlSr2Br5 is about 19,000 and 37,000 ph/MeV, respectively. This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number 20CWDARI00036-01-00. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

Invited Talk

Extreme Helical Morphology Exhibited by Iodinated Phenanthroline Crystals

Christopher Grainger (University of Bristol)

Keywords: Growth; Low Dimensional, Helical; Iodinated; Solution Growth; Twisted Crystal; Optical Materials, Quantum Materials

Crystals exhibiting strong helical morphology have been crystallised from an Iodinated solution of Phenanthroline. Modifications were made to the crystallisation procedure of catena-[tris(1,10-phenanthrolin-1-ium) heptaiodide 1,10-phenanthroline solvate] (CCDC number 2041514), first grown by T. PorÄ™ba, M. Swiatkowski, R. KruszyÅ„ski in 'Experimental Crystal Structure Determination', 2021, (DOI: 10.5517/ccdc.csd.cc26jc9f). The altered procedure, combined with a healthy portion of serendipity, led to the growth of the helical crystals presented. Characterisation past preliminary EDX spectra is being undertaken to confirm the structure of said helical crystals. When SEM images were shown to Prof Kahr, he recommended I submit this abstract and attend the Symposium.

Invited Talk

Bowties vs Mantis Shrimp. Who can rotate the polarization of light better?

Prashant Kumar (Characterization)

Keywords: Characterization, Growth; 2D; Oxides; Solution Growth; Twisted Crystal; Optical Materials

Humans can barely detect polarization of light, on the other hand, crustaceans like mantis shrimp utilize circular polarization of light to communicate with each other. The unique arrangement of microscopic elements in their shell rotates the polarization of light enabling them to hunt and defend themselves. Inspired by this ability of nature, I will demonstrate how three-dimensional chiral structures can be used as coatings for encoding the polarization of light at desired wavelengths. Micron-sized particles resembling the shape of bowties are self-assembled from anisotropic building blocks of cadmium-cystine complexes with widely variable geometry, chirality measures and optical asymmetry while retaining consistent twisted shapes [1]. Electron microscopy, X-ray diffraction (XRD), and circular dichroism spectroscopy reveal four levels of hierarchical organization within the cadmium-cystinate bowties. Scanning electron microscopy (SEM) images for the terminal and intermediate stages of the synthesis show that bowties (level 4) are structured as a stack of twisted nanoribbons 200 â€“ 1200 nm in length and 45 nm in thickness (level 3). The nanoribbons are assembled from nanoplatelets (level 2) 50 â€“ 200 nm in length and a thickness of ~1.2 nm calculated from the solved crystal structure. Using synchrotron XRD, vibrational circular dichroism spectroscopy, and Rietveld refinement, I resolve the chiral conformations of the smallest building block (level 1) of cystine molecule bonded to cadmium in atomic detail and correlate it with the sharp peaks in radially averaged cryo-SAED patterns. The nanoribbons and bowties are guided to acquire progressively stronger twists as the enantiomeric excess (Â±Ï‡) of L- or D-CST increases to demonstrate the emergence of a chirality continuum in bowties transitioning from a left-handed twist to flat pancakes to a right-handed twist. The self-limited self-organization of anisotropic building blocks driven by a competition between electrostatic and van-der-Waals interactions makes possible high synthetic reproducibility and computational predictability of the geometries for different concentrations of reagents, ionic components, enantiomeric compositions, media polarity and other parameters. I correlate the multitude of bowtie shapes with their unique spectral fingerprint in near-IR range to predictively design 3D chiral shapes and use them as coatings on glass, plastic, and cloth. Furthermore, the application of these coatings as markers for machine vision where they preferentially reflect circularly polarized light originating from a LIDAR device is demonstrated. [1] Kumar, P., Vo, T., Cha, M. et al. Photonically active bowtie nanoassemblies with chirality continuum. Nature 615, 418â€“424 (2023). https://doi.org/10.1038/s41586-023-05733-1

Invited Talk

Twisted Organic Semiconductor Crystals

Stephanie Lee (New York University), **Bart Kahr** (New York University), **Alexander Shtukenberg** (New York University), **Sehee Jeong** (New York University), **St. John Whittaker** (New York University), **Yongfan Yang** (New York University)

Keywords: Characterization, Devices, Growth; Thin Film; organic; Melt Growth; Twisted Crystal; Energy Materials

Molecular crystals that twist as they grow are common but little known and introduce completely unexplored features to materials design. Here, we present growth-induced twists to molecular semiconductor crystals with the expectation that microstructure and continually precessing crystallographic orientations can modulate interactions with photons and electrons. We have found that a variety of organic semiconductors and charge transfer complexes can be readily induced to grow from the melt as spherulites of tightly packed helicoidal fibrils. The twisting pitch can be controlled by the degree of undercooling after melting or through the incorporation of additives. Because twisting exposes different crystallographic faces at the film/air interface, some with higher conductivity than others, twisted organic semiconductor films exhibit higher charge mobilities and photoconductivites compared to their straight counterparts. Photoluminescence intensity is also modulated by crystal twisting, with some orientations exhibiting stronger PL signal compared to others. Solubility differences between different crystallographic faces can also be used to pattern films on the tens of microns length scale. These results indicate crystal twisting to be a promising strategy for modulating the performance ofl optoelectronics.