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Carolina Science Symposium

2019

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### Awards

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<td>2 awards for the best paper published during the year that acknowledges the use of the Analytical Instrumentation Facility sponsored by AIF</td>
<td>$200/ea</td>
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<td>RTNN Student Oral 1st Prize</td>
<td>For the best student oral presentation sponsored by RTNN</td>
<td>$200</td>
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<td>Student Poster 1st Prize</td>
<td>Sponsored by AVS Mid-Atlantic</td>
<td>$500</td>
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<td>Student Poster 2nd Prize</td>
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<td>2 presented Sponsored by Kurt J. Lesker and All Scientific</td>
<td>$100/ea</td>
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<td>Best poster that shows X-ray Diffraction techniques</td>
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<td>Sponsored by Asylum Research</td>
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<td>$50/ea</td>
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<td>CSS Raffle</td>
<td>1 Drawing randomly from attendees that have filled out the online survey after the meeting.</td>
<td>$50</td>
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<td>AIF, NCSU</td>
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<td>Edwin Dickinson</td>
<td>NCSU</td>
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<td>Taylor Teitsworth</td>
<td>Student, UNC</td>
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<td>NCSU</td>
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<td>NCSU/AIF</td>
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Speakers

**Virtual Anatomy: Applications of tomography and digital modeling to quantify form and function**

**Edwin Dickinson**

Recent innovations in imaging technologies are facilitating a revolution in comparative anatomy, enabling micro- and nano-scale observations of biological phenomena. As such, a significant portion of anatomical research now exists in digital space. Using novel imaging techniques such as contrast-enhanced tomography, we are capable of quantifying and modeling fine detail in soft tissues. We will demonstrate some of the cutting-edge applications of these technologies across biological disciplines, and demonstrate the myriad applications of these imaging modalities to enhancing our understanding of anatomical form and function.

[edwin_dickinson@ncsu.edu](mailto:edwin_dickinson@ncsu.edu)
Particle suspension reactors (PSRs) are an inherently cheap architecture for solar water-splitting that could enable cost-competitive solar fuels. Due to the energetic requirements of water splitting, most nanoparticles demonstrated for use in PSRs are wide-bandgap materials that require short wavelength light (<500 nm). However, multijunction silicon nanowires (MJ SiNWs) produce photovoltages that are not limited by the bandgap while retaining the absorption properties of a low-bandgap material. Using a highly-controlled bottom-up synthesis, we have realized MJ SiNWs for the first time. Single nanowire photovoltaics show a linear increase in photovoltage as the number of junctions is increased, exceeding 10 V with 40 junctions. Our MJ SiNWs are capable of facilitating photooxidation and photoreduction of metal ions to spatioselectively deposit metal and metal oxide catalyst materials onto the wires. Microfabrication of single NW electrochemical cells has allowed us to measure the photoelectrochemical behavior of the functionalized wires in solution. These wires are then dispersed into prototype PSRs where we measure hydrogen production as a function of wavelength, illumination intensity, and number of junctions.

tayb@live.unc.edu
The fabrication of high purity copper using additive manufacturing has proven difficult because of oxidation of the powder feedstock. Here, we present work on the hydrogen heat treatment of copper powders for electron beam powder bed fusion (EB-PBF), in order to enable the fabrication of high purity copper components for applications such as accelerator components and vacuum electronic devices. Copper powder with varying initial oxygen contents were hydrogen heat-treated and characterized for their chemistry, morphology, and microstructure. Higher initial oxygen content powders were found to not only reduce surface oxides, but also reduce oxides along the grain boundaries and form trapped H2O vapor inside the particles. The trapped H2O vapor was verified by thermogravimetric analysis (TGA) and residual gas analysis (RGA) while melting. The mechanism of the H2O vapor escaping the particles was determined by in-situ SEM heated stage experiments, where the particles were observed to crack along the grain boundaries. To determine the effect of the EB-PBF processing on the H2O vapor, the thermal simulation and the validation of single melt track width wafers were conducted along with melting single layer discs for chemistry analysis. A high speed video of the EB-PBF melting was performed in order to determine the effect of the trapped H2O vapor on the melt pool. Finally, solid samples were fabricated from hydrogen-treated copper powder, where the final oxygen content measured ~50 wt. ppm, with a minimal residue hydrogen content, indicating the complete removal of trapped H2O vapor from the solid parts.

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Analysis of permethrin treated fabric using tof-sims
Chuanzhen Zhou, Fred A. Stevie, Roberto Garcia

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Insecticides are commonly applied to garments to protect the wearer from insect attack. This is becoming more important as diseases such as West Nile Virus, which is spread by mosquitoes, have become more common. Recent studies have shown it is possible to use ToF-SIMS to identify and quantify mosquito insecticides, such as permethrin and deltamethrin, on mosquito netting. [1-2] In this case, the insecticide is infused into high density polyethylene. Once the insecticide at the surface is depleted, insecticide in the netting can diffuse towards the surface and become bioavailable for the mosquito to acquire upon physical contact. Another area of study is mosquito repellent clothing, which is made from fabric topically treated with insecticide. After a certain number of washing cycles, the clothes will no longer be effective to repel mosquitoes. Currently, two approaches are used to evaluate the insecticide content and potency of insect repellent garments. One is standard chemical analysis using solvent extraction followed by chromatography to determine the total insecticide content. However, this cannot distinguish the bioavailable fraction. The other is mosquito bioassays which directly measure the ability of the garments to knock down mosquitoes, but these measurements are error-prone, time-consuming, and require a rearing facility to produce large volumes of mosquitoes for testing. It is essential to find an alternative way to directly measure the amount of insecticide bioavailable on the surface of a garment. ToF-SIMS appears to be the right technique to achieve this goal. This technique can distinguish cotton and Nylon and can identify permethrin which is the only insecticide currently approved for garments. In this study, ToF-SIMS analyses have been made on cotton/Nylon based fabric surface and ultramicrotomed cross sections before and after 10 and 30 washings to measure the reduction in insecticide. The amount of insecticide was dramatically reduced after 30 washings. Cross section analysis showed the penetration of the insecticide in the fabric. Interestingly, the results of fabric cross sections show a significant decrease of insecticide in cotton fibers but slight decrease in Nylon fibers after 10 washings. After 30 washings, the amount of insecticides was reduced roughly by 6 fold for both Nylon and Cotton fibers. We know that the 30 washings sample was no longer effective against mosquitoes. The results have implications for the amount of acceptable washings for mosquito repellent fabric.
Figure 1. Negative ion ToF-SIMS overlaid images of C3H3O2- (in red for cotton fiber), Cl- (in green for permethrin) and CN- (in blue for Nylon fiber) on permethrin treated clothing ultra microtomed cross sections before and after 30 washings. Field of view: 100 μm x 100 μm.

References


Mechanical Properties of Nanoscale Collagen Mimetic Peptides via Molecular Dynamics

Atul Rawal, Kristen L. Rhinehardt, Ram V. Mohan.

Collagen is a pervasive, triple helical, extracellular matrix (ECM) protein, found in human body from skin and bones to blood vessels and lungs, making it biocompatible, biodegradable, capable of cell attachment, and relevant for applications in bio-polymers, tissue engineering and a plethora of other bio-medical fields. Natural collagen's extraction from natural sources is time consuming, sometimes costly, and it is difficult to render, and could present undesired biological and pathogenic changes. Nanoscale collagen mimetic peptides (Synthetic Collagen), without the unwanted biological entities present in the medium, has shown to mimic the unique properties that are present in natural collagen. Synthetic collagen, thus provides a superior alternative compared to natural collagen for its utilization in several applications. Their properties are affected by surrounding environments, including various solvents, and can be tailored toward specific applications. The focus of this study is to investigate the mechanical properties of these nanoscale collagen mimetic peptides with lengths of about 10nm, leading to understanding of their feasibility in bio-printing of a composite polymeric collagen biomaterial with a blend of multiple synthetic collagen molecules. Molecular dynamics modeling is used to simulate, model and analyze mechanical properties of two different synthetic collagen peptides, with a varying amino acid content. In particular, mechanical behavior of these peptides are studied. An in-depth insight into the deformation and structural properties of the collagen peptides are of innovative significance for a multitude of bio medical engineering applications. Present study employed steered molecular dynamics as the principal method of investigating the mechanical properties of nanoscale collagen mimetic peptides 1BKV, which closely resembles natural collagen with a shorter sequence length of 30 amino acids, and collagen mimetic peptide 2CUO, which has a different amino acid concentration. A detailed comprehension of the protein's mechanical properties is investigated through fraying deformation behavior studied. A calculated Gibbs free energy value of 40 Kcal/mol corresponds with a complete unfolding of a single alpha-helix peptide chain from a triple helical protein in case of fraying. Force needed for complete separation of the alpha-helix from the triple-helical protein is analyzed, and discussed.

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Intelligently-Tuned Silicon Nanowire Geometric Diodes for Energy Harvesting

James Custer, Jeremy Low (UNC physics), Taylor Teitsworth, Dr. David Hill, Dr. Joseph Christesen (UNC Chemistry), Dr. James McBride (Vanderbilt), Collin Mckinney (UNC Electronics Core), Dr. Martin Brooke (Duke EE), Dr. James Cahoon (UNC Chemistry)

Geometric diodes operate by causing charge carriers to flow more easily in a forward direction than a reverse direction simply based on the shape of the structure. Thus, the structure is able to ratchet charges (like a socket wrench ratchets motion). The ratcheting of charges manifests itself in the ability to rectify an alternating current (AC) and generate a non-zero output voltage. Traditional diodes, such as P-N junctions or Schottky barriers, rely on a potential barrier to produce rectification; however, geometric diode's lack of a potential barrier gives them a twofold advantage over traditional diodes. 1) They can be truly zero-bias diodes because there is no potential to overcome. 2) Their capacitance can be ultra-low (~10E-18 F), giving them a theoretical frequency response of ~1 THz. The combination of these traits makes them useful as simultaneous high-speed (>10 GHz) wireless signal processors and long-wavelength energy harvesters, enabling battery-less internet-of-things devices and sensors.

In this work, geometric diodes have been created from etched silicon nanowires. The wires are grown and encoded with dopants using the vapor-liquid-solid mechanism in a chemical vapor deposition system. Following the growth, a dopant-selective wet-chemical etch is used to create the desired “sawtooth” nanostructure. Metal contacts are connected to the wires using electron-beam lithography and evaporation enabling direct current (DC) and AC measurements. The etched wires produce asymmetric, diode-like current-voltage (I-V) curves at DC. The device performance and I-V characteristics can be intelligently tuned using the wire's geometry and surface. Rectification of an AC signal has been measured up to 40 GHz, confirming the wires ability to ratchet charge carriers at high frequency and function as a high-speed signal processor and energy harvester.

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Enhanced Darkfield Hyperspectral Imaging System as an Analytical Tool to Distinguish Between Monolayer, Few-layer and Multilayer MoS2
Investigating the Effects of Growth Conditions on Superconductivity in Titanium Oxide Thin Films

Yasemin Ozbek, Cooper Brooks

Superconductivity is a well-known and sought-after phenomenon in solid state physics, yet scientists are still struggling to explain all of the intricate conditions needed for it to occur. Recent reports indicate a superconducting transition at 8 K for an orthorhombic phase of titanium oxide thin films grown by pulsed laser deposition above a critical thickness of ~100 nm. These results indicate an intricate relationship between film thickness, crystal structure, and superconductivity. To investigate this relationship, we study titanium oxide (TiO\textsubscript{2}) films grown by Molecular Beam Epitaxy (MBE) on sapphire (AlO\textsubscript{2}) substrates as a function of film thickness and growth oxygen pressure. The structural properties of the samples will be determined using X-Ray Diffraction (XRD), Raman Confocal Microscopy (RCM), and Atomic Force Microscopy (AFM). Temperature-dependent transport measurements from 2 K to 300 K will be used to determine the superconducting transition temperature of the films. By correlating the growth conditions, atomic-scale structure, and superconducting properties of the titanium oxide films, the underlying physical mechanisms which stabilize superconductivity will be established. These results will aid in the experimental and theoretical discovery of new superconductors with high transition temperatures.
Structural Characterization of Cobalt Ferrite and Hafnia Interface Annealed at Various Temperatures

Alexandria Cruz, Eric Vetter, Dr. Chuanzhen Zhou, Dr. Christopher Winkler, Dr. Jacob Jones

Magnetoelectric (ME) composites potential to be used in everyday technology. For example, in cell phones they have potential as electric current sensors, attenuators, circulators and signal filters. ME composites are made of two parts: a magnetostrictive (MS) phase and a piezoelectric (PE) phase. MS materials are interesting because when they are stretched or compressed, they generate a magnetic field. Conversely, MS materials deform in a magnetic field. The key to good magnetoelectric composites is the MS and PE interface for strain coupling $k_c$. $k_c$ is the coupling factor ($0 \leq k_c \leq 1$) between the MS and PE phases. In other words, $k_c$ describes how well strain transfers from one material to the other material. Thus, the interface must be chemically stable, not have interfacial diffusion and not form any secondary phases. This research investigates an ME composite of cobalt ferrite (CFO) and Hafnia (HfO2), a new combination of materials that has not previously been explored in the literature.

Hafnia is a relatively new ferroelectric material that exhibits ferroelectricity on length scales less than 10nm making hafnia optimal for size minimization, unlike other ferroelectric materials. For example two commonly used ferroelectric materials, BaTiO3 and PZT, lose their ferroelectric properties when films are thinner than 130nm. The drawback to Hafnia is its low piezoelectric coefficient of 10 pC/N while BaTiO3 and PZT have piezoelectric coefficients of 191 and 590 pC/N respectively. A low piezoelectric coefficient would cause a low magnetoelectric coefficient. In this work, hafnia deposition was performed via atomic layer deposition to better control the sample film thickness.

Cobalt ferrite is the most magnetostrictive material ($\lambda_{100} = -590$ppm) without any rare earth elements. CFO is electrically insulating, chemically robust, and can be deposited multiple ways. Sputtering was selected for the deposition method because of its repeatability, making multiple samples at once, and the ability to easily texture CFO.

Three samples of CFO/ HfO2/SiO2/Si were fabricated and each sample was annealed at a different temperature: unannealed, 500°C for 60s, and 800°C for 60s. X-ray diffraction was used to determine the crystallinity of the phases. Time of flight secondary mass ion spectroscopy was used to evaluate diffusion among the tree samples. Transmission electron microscopy was used to image cross-sections of the samples. Electron dispersive spectroscopy was used to map out the elements in the cross-sections of the samples.
This work discusses a novel method of production of a liquid metal eutectic gallium-indium (EGaIn) thin film on a copper substrate through electrophoretic deposition (EPD). The EPD process involved an electric field in the range of 200-250 V/cm, with a charging salt (MgSO4) concentration of 0.108 M and an EGaIn nanoparticle concentration of 0.03 g/L in an isopropyl alcohol solution. This experiment formed a conductive liquid metal layer approximately 10-20 µm high with a naturally forming solid oxide skin, which adds mechanical stability. The oxide skin also adds self-healing capabilities to the thin film by being able to reform immediately after rupturing. Optical profilometer analysis revealed a rough surface morphology due to the presence of the oxide layer. Thin film thickness was strongly connected to EGaIn concentration in solution, charging salt concentration, environmental temperature and EPD duration. Specifically, film thickness was directly correlated to EGaIn concentration and EPD duration. This work has implications in flexible electronics and other circuitry as a novel self-healing and conductive agent to repair damaged electrical circuits.
Observing Optical Bound States in the Continuum in Silicon Nanowire Superlattices through Photothermal Spectroscopy

Sarah E. Morley, Seokhyoung Kim, and James F. Cahoon

Optical bound states in the continuum (BICs) are the subject of much scientific interest due to the very improbability of their existence. As the name suggests, BICs are optical modes which exist within the spectral continuum, but are perfectly confined and entirely decoupled from the surrounding waves. BICs have been proposed and to some extent observed in a number of macroscopic and two-dimensional systems. However, the creation of optical BICs in one-dimensional, laterally confined structures is as yet unexplored. Silicon nanowires (NWs) are an attractive 1D medium thanks to the combination of vapor-liquid-solid (VLS) growth and dopant-dependent chemical etching. Using this technique, we can create diameter-modulated NW geometric superlattices (GSLs) with sub-10 nm morphological resolution, which have previously been demonstrated to display unique optical properties. Here, we elucidate the presence of BICs in a NW GSL and illustrate the creation of high-quality-factor (high-Q) optical cavities through finite-element modeling and a novel application of photothermal spectroscopy.
Solvent-free spin-casting of single-crystalline hybrid perovskite microstructures by controlling deliquescence and efflorescence

Jonathan K. Meyers, Lorenzo Y. Serafin, and James F. Cahoon

Lead halide perovskites (LHPs) continue to rise with promise for efficient optoelectronic applications including photovoltaics, light-emitting diodes, and lasers. A wide variety of deposition techniques and treatments have been developed for LHPs with the goal of improving crystallization and thus efficiency and stability. Of particular interest to us is the exposure of perovskite films to methylamine gas. Such treatment has been shown to liquefy the film and dramatically decrease grain boundary defects in the treated film, especially at elevated temperatures. To better understand this reaction, we applied in-situ UV-visible spectrophotometry in controlled conditions of temperature and methylamine gas pressure to obtain a quantitative phase diagram highlighting solid, solid intermediate, and liquid phases and identified this process as a form of deliquescence and efflorescence. In this presentation, we discuss the impact of forcing crystallization along paths through this phase diagram. Additionally we stress the importance of the liquid-substrate interaction as evidenced by contact angles measured between liquid perovskite and various substrates. Lastly, we demonstrate the utility of these findings in a unique demonstration of solvent-free spin-casting of liquid perovskite into single-crystalline microstructures.
Sustained release of Diclofenac Sodium from electrospun biocompatible composite nanofibers of Poly(ε-caprolactone)/Chitosan

Sheikh Saudi, Narayan Bhattarai

Electrospun nanofibers have been found as a versatile platform to deliver different doses of physicochemical diverse agents. However, there is still an unmet need to develop practical fiber compositions for water-soluble drugs needed at high dosing or desire for sustained release doses. To date, most sustained release electrospun fibers have been mostly restricted to the delivery of hydrophobic drugs at low drug loading which is often not beneficial in some clinical applications. For hydrophilic, small molecule drug, such as Diclofenac Sodium (DS) due to its high aqueous solubility and poor incompatibility with insoluble polymers, makes long-term release even more challenging. Here we investigate electrospun composite nanofibers of poly (ε-caprolactone) (PCL) and chitosan (CS) to sustain release of DS drug that are highly loaded in the fibers. Nanofibers with different amount of DS drug were synthesized by Electrospinning technique. Different physicochemical properties such as morphology, aqueous stability, crystallinity, mechanical properties, chemical structure were studied, and cellular compatibility were evaluated. High drug entrapment efficiency and concentration dependent drug release patterns were obtained in phosphate buffered saline up to 14 days.
A Novel Predictive Design Approach to Tailor Band Structure of Metal-Organic Framework Nanocrystals in One-Dimensional Periodic Array

Sujoy Saha, Joseph Starobin, Hemali Rathnayake

The study of band structures of different types of Metal-Organic Frameworks (MOFs) is indispensable for the advancement of nano-electronics technologies. We design a novel approach to predict and tailor the band structure of MOFs nano crystals in one-dimensional (1-D) periodic array through the variation of structural and materials parameters. From the Bloch condition of Schrodinger equation, we could predict amplitude of potentials, $\alpha$ and $\beta$ for periodically arranged MOFs only in one-dimension using experimental values of dielectric constant, absorption and emission peaks of MOFs. Predicting energy band structures of the one-dimensional array of Zn MOFs from a theoretical method combined with experimental values of $\beta$ is a unique combination of scientific research, which could provide insight into electronic band energy to tailor optoelectronic properties of MOFs and understanding their energy transfer capabilities. The dielectric constants of three different MOFs synthesized from the same metal precursor (Zn$^{2+}$) and three ligands (organic dicarboxylic acids) with different lengths of aromatic rings are calculated from measuring the capacitance and materials thin film thicknesses. Band gap depends on the $\beta$ value, which is a function of the length of the ligand of a MOF and dielectric constant. Thus, the length of ligands in MOFs have a significant impact on the jumps between two allowed bands in energy band structures of the 1-D array of MOFs as these jumps depend on the band gaps. This predictive design method can widely applicable for predicting band energy for any designed MOFs and serves as a versatile tool to tailor and predict electronic properties.
Vertical Yield and Pitch Dependency in Patterned GaAsSbN Nanowires

Sean Johnson, Rabin Pokharel, Michael Lowe, Dr. Jia Li, and Dr. Shanthi Iyer

Vertically grown nanowires are a research interest in optoelectronics and photovoltaic applications due to their high surface to volume ratio and good light trapping capabilities. This study presents the effects of process and design parameters on of self-catalyzed GaAsSbN nanowires grown by plasma-assisted molecular beam epitaxy on patterned silicon substrates using electron beam lithography. Results via scanning electron microscopy show the sensitivity of patterned nanowire growth to the parameters of nanowire diameter, pitch, dose time, etching techniques and growth plan. Diameters range from 90 nm to 250 nm. Pitch is compared for values ranging from 200 nm to 1200 nm at each diameter. Dry etching of the oxide layer of the silicon substrate and PMMA coating is performed using reactive ion etching for 20 s and 120 s respectively. Comparisons of different HF etch times performed pre and post PMMA removal are presented. Photoluminescence results show the effect of pitch on the optical characteristics of the nanowires.

This work is financially supported by National Science Foundation (Award No. 1649517).
In this work, unique properties of dilute nitride GaAsSbN material system and different architecture in nanowire configuration are exploited to achieve 1.3 μm photoluminescence (PL) emission wavelength. NW based photodetectors in this wavelength range are of great interest for next generation single-photon sources and photodetectors for quantum networking, nanophotonic integrated circuits and solar cell applications. Here, we report high density of axial GaAsSb/GaAsSbN NWs on Si (111) substrate with reduced bandgap energy and improved optical properties. GaAs passivating shells was used to reduce non-radiative surface recombination in axial configuration. Molecular beam epitaxy is the enabling technology that has been used to realize Ga-catalyzed nanowires in axial configuration.

In our previous work [1, 2], GaAsSbN core-shell NWs exhibited high density NWs, while in axial configuration red-shifting the emission wavelength to 1.3 μm resulted in tremendous decrease in NW density. Furthermore, the PL spectra of dilute nitride nanowires were significantly less than the non-nitride nanowires, indicating defects and traps within nanowire structure severely degrading optical quality. In this work, our focus has been to increase NW density and improve PL intensity in axial configuration, retaining the high quality of nanowires. We demonstrate the approaches of controlled exposure of RF N-plasma to NW growth and axial inserts of GaAsSbN in GaAsSb nanowires with appropriate timing of the nitrogen firing, nanowire density can be increased significantly along with improved 4K and room
temperature PL characteristics. Red shifts in both the LO and TO Raman modes as well as PL characteristics in nitrides with respect to the non-nitride nanowires attest to the nitrogen incorporation in these NWs. Transmission electron microscopy was used to study defects and crystal structure in the axial inserts configured NWs with zincblende crystal structure. Thus, this work shows GaAsSbN to be a promising material system in the NW configuration with potential for further red-shifting photodetection capability to 1.55 μm.

Acknowledgements

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Study of conduction mechanism in GaAsSb nanowires and the effect of in-situ annealing in ultra-high vacuum

Mehul Parakh, Sean Johnson, Rabin Pokharel, Priyanka Ramaswamy, Surya Nalamati, Jia Li and Shanthi Iyer

In this work, the first observation of the space charge limited conduction mechanism (SCLC) in GaAsSb nanowires (NWs) grown by Ga-assisted molecular beam epitaxial technique, and the effect of ultrahigh vacuum in-situ annealing have been investigated. The low onset voltage of the SCLC in the NW configuration has been advantageously exploited to extract trap density and trap distribution in the bandgap of this material system, using simple temperature dependent current-voltage measurements in both the ensemble and single nanowires. In-situ annealing in an ultra-high vacuum revealed significant reduction in the trap density from 1016 cm\(^{-3}\) in as-grown NWs to a low level of 7 \(\times\) 1014 cm\(^{-3}\) and confining wider trap distribution to a single trap depth at 0.12 eV. A comparison of current conduction mechanism in the respective single nanowires using conductive atomic force microscopy (C-AFM) further confirms the SCLC mechanism identified in GaAsSb ensemble device to be intrinsic. Higher current observed in current mapping by C-AFM, increased 4K photoluminescence (PL) intensity along with reduced full-width half maxima and more symmetric PL spectra, reduced asymmetrical broadening and increased TO/LO mode in room temperature Raman spectra for in-situ annealed NWs again attest to effective annihilation of traps leading to the improved optical quality of NWs compared to as-grown NWs. Hence, the I-V-T analysis of the SCLC mechanism has been demonstrated to be a simple approach to obtain information on growth induced traps in the NWs.
I-V Characterization of GaAsSb(N) Single Nanowire using Non-Destructive Technique, Conductive Atomic Force Microscopy (C-AFM)

Priyanka Ramaswamy¹, Rabin Pokharel², Shisir Devkota², Surya Nalamati¹, Jia Li², and Shanthi Iyer².

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Nanowires, a one-dimensional semiconductor nanostructure, have paved way for the bandgap engineering of the alloy systems for the fabrication of wide range of IR photodetectors. It is evident that the photodetectors demonstrate selective wavelength dependence for response per unit incident radiation power. The advantage of photon detectors over thermal detectors are good signal to noise ratio and responsivity. In recent times, the development in the exploration of the photoconduction mechanism of high density of surface states low-dimensional systems have attracted researchers to work on the potential application of nanowires such as photosensing elements in highly integrated optoelectronic devices, transceivers, and optical interconnects. The most promising candidate amongst the semiconductors is considered to be the GaAs1-xSbx for the application in optical telecommunication, NIR sensing etc., due to their capability of bandgap tuning between 870 nm and 1700 nm.

In this work, photoresponse of intrinsic GaAsSb, n- doped GaAsSb and GaAsSbN nanowires on p-Si (111) and graphene/SiO2/p-Si (111) substrates which are grown by molecular beam epitaxy (MBE), are compared using conductive atomic force microscopy (C-AFM). C-AFM is a versatile, time-efficient, simple and non-destructive powerful technique for characterizing electrical properties of nanowires. C-AFM is also found to be advantageous for I-V characterization of single nanowire compared to ensemble as there is no processing such as spin coating, plasma etching, deposition of metals for contacts is involved. We investigated the topographical and electrical characteristics of vertical single nanowire on p-Si (111) and graphene/SiO2/p-Si (111) substrates using C-AFM. Further, responsivity and external quantum efficiency of various nanowires are compared using current-voltage characteristics.
Graphene Platform for Ga-assisted GaAsSb Nanowires Grown by Molecular Beam Epitaxy

Surya Nalamati, Priyanka Ramaswamy, Kendall Dawkins, Jeffrey Kronz, Robert Lavelle, David Snyder, C. Lewis Reynolds. Jr., Matthew Cabral and Shanthi Iyer

We report the successful growth of high-quality GaAs$_{1-x}$Sbx nanowires on monolayer graphene/SiO$_2$/p-Si (111) using molecular beam epitaxy (MBE) for the application of a flexible near-infrared photodetector. A systematic and detailed study of NW growth parameters, namely, growth temperature, V/III beam equivalent pressure (BEP) ratio, and Ga shutter opening duration, has been carried out. Growth of vertical <111> oriented nanowires on graphene with 4 K photoluminescence emission in the range 1.24–1.38 eV has been achieved. The presence of a weak D mode in Raman spectra of NWs grown on graphene suggests that NW growth did not alter the intrinsic properties of the monolayer graphene. High-resolution transmission electron microscopy and a selective area diffraction pattern confirmed the zinc-blende crystal structure of the NWs. This study suggests that Sb as a surfactant plays a critical role in the surface engineering of the substrate, leading to the superior optical quality of NWs exhibiting a higher 4 K photoluminescence intensity and lower full width at half maxima (fwhm) with significant improvement in optical responsivity compared to NWs grown on Si substrate of similar Sb composition. Novel growth conditions for improvement of NW density and device performance will be discussed.
Electrostatics of Radial P-I-N Core-Shell GaAsSb and GaAsSb(N) Nanowires

Kendall Dawkins, Rabin Pokharel, Shanthi Iyer

In this work, the electrostatic mapping of radial core-shell P-I-N GaAsSb and GaAsSb(N) nanowires is carried out using COMSOL Multiphysics Modeling Software. These simulations can be used as a tool in pre-growth studies to determine the best fabrication methods needed to provide desired characteristics. GaAsSb and GaAsSb(N) is among the mixed As-Sb- based III-V material system that covers the important wavelength range from 870 nm to 1700 nm, which has potential applications in next generation optoelectronic devices namely solar cells, optical telecommunications, and photonic integrated circuits. The simulation models show that the built-in electric field of the p-i-n radial nanowire reaches its maximum in the region where the i-layer adjoins the core no matter the material that is being used. When moving away from the i-layer center, electric field steadily decays. A systematic approach has been carried of varying core thickness, shell thickness, and doping concentration to understand how electric field varies as each parameter change. Results show that with increased doping, maximum electric field increase as well until a certain concentration is reached where the maximum electric field starts to plateau. Our results show that core and shell thickness also are critical in achieving the maximum thickness.

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GaTe as N-Dopant Source for GaAs Nanowires Grown by Ga Assisted Molecular Beam Epitaxy

Shisir Devkota1, Mehul Parakh1, Priyanka Ramaswamy2, Kendall Dawkins1, Lew Reynolds, Matthew Cabral4 and Shanthi Iyer1

N-type doping of GaAs nanowires (NWs) grown by molecular beam epitaxy (MBE) on (111) Si substrate using gallium telluride (GaTe) as a dopant source is successfully reported. A detailed study has been carried out to assess the impact of variation of GaTe source cell temperature on morphology, electrical and optical properties of NWs. Tellurium (Te) doping in the NWs was investigated for GaTe cell temperatures ranging from 200°C to 570°C. The variations in the optical, electrical and morphological characteristics with cell temperature were investigated using low-temperature photoluminescence (PL), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Te incorporation in our NWs was attested by the presence of 4K PL shoulder peak, which is 0.18 eV red shifted with respect to GaAs band to band transition at 1.50 eV. Moreover, a shift in the PL peaks, variation in their full width maxima and corresponding variation in the I-V characteristics from AFM were used to ascertain the increase in Te incorporation in the NWs with increasing cell temperature. Best fitting of the simulated I-V curves with the experimental data on a single NW obtained from AFM yielded the highest carrier concentration of 2.2*10^17/cm^3 with a carrier mobility of 7500 cm^2/Vs. The highest responsivity of Te doped NW/p-Si was found to be 64 mA/W. Transmission electron microscopy (TEM) investigations of these NWs will also be presented.
Designing a Coded Aperture Cycloidal Mass Analyzer to Detect Perfluorocarbon Tracers

Kathleen Horvath\textsuperscript{1}, Tanouir Aloui\textsuperscript{1}, Raul Vyas\textsuperscript{1}, Maria Luisa Sartorelli\textsuperscript{1}, Jason J. Amsden\textsuperscript{1}, Jeffrey T. Glass\textsuperscript{1}, Roger P. Sperline\textsuperscript{2}, M. Bonner Denton\textsuperscript{2}, Jesko A. von Windheim\textsuperscript{3}, David Koester\textsuperscript{3}, Patrick Keelan\textsuperscript{4}, Yuriy Zhilichev\textsuperscript{5}

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High voltage transmission cables (HVTCs) exist buried underground as part of the electrical utility grid. These HVTCs degrade over time and the petroleum-based dielectric fluid can leak into the surrounding environment posing a safety, economic, and environmental concern. Current HVTC leak detection methods involve injecting perfluorocarbon tracer (PFT) molecules into the dielectric fluid and detecting PFT with a custom modified gas chromatograph mounted in a truck. The gas chromatograph is extremely sensitive, but suffers from poor dynamic range, high cost, and limited portability. Duke University is collaborating with PFT Technology to develop a cycloidal coded aperture portable mass spectrometer capable of detecting PFT molecules for locating leaks in HVTCs in the field. This work presents a preliminary design and finite element analysis simulations of the proposed cycloidal mass analyzer including a 0.7 T NdFeB magnet, aluminum electric sector, electron ionization source, and focal plane capacitive transimpedance amplifier array detector. The mass analyzer is designed to detect fragments of PFT molecules in the mass range of 59-160 amu with a resolution of 0.5 amu. The anticipated footprint of this mass analyzer is 30 cm x 27 cm x 11 cm and will weigh ~ 40 kg.

Nirmalay Barua, Ingrid M. Padilla Espinosa, Ram V Mohan

Boron Nitride Nanotubes (BNNT) have been a viable candidate in the nanodomain research era due to their unique combination of structural, electrical and chemical properties. Their potential application in nanofabrication has yet not been explored due to the difficulties in property evaluation at a nanoscale level. The lack of comprehensive experimental methods to study the fundamental properties of materials can be overcome with the help of computational techniques. In this study a classical finite element method scheme has been adapted to understand the interactions at an atomic scale and their outcome on the overall materials property. The Tersoff-Brenner potential is employed to define the computational structure and interaction between boron and nitrogen atoms. Young’s modulus, bulk modulus, poison’s ratio are evaluated for these nanotubes. The effects of length and chirality on their thermo-elastic properties are analyzed as well. The simulation result yields a co-relation between young’s modulus and chirality while the bulk modulus remain unaffected.
Assembly and Configuration of Variable Temperature Scanning Tunneling Microscopy (STM) System

Michael Lowe, Dr. Jia Li, Dr. Shanthi Iyer

The scanning tunneling microscope (STM) is a very sophisticated and sensitive instrument that requires high accuracy at the atomic level and consists of many different systems including an ultra-high vacuum chamber with extreme vibration isolation and a very fine conducting tip that is brought close to the sample to measure the current of the tunneling electrons when a bias is applied between the two. From being able to select a suitable vibration isolated environment and a sufficient mounting surface to the configuration of the entire pumping system and the setup of the computer system, the assembly of an STM system takes a high level of patience and accuracy to be able to get all of the delicate systems working together properly in order to provide an image with resolutions high enough to detect individual atoms.
With a growing demand for continuous miniaturization and functional scaling, the complementary metal-oxide semiconductor (CMOS) platform continues to drive advances in integrated circuits (IC), nanoelectronics and information processing technologies. Directed self-assembly of block copolymers is the current state-of-the-art which yields patterns with various morphologies and could reach minimum feature size up to 8 nm. In order to continue Moore’s Law further to take new nodes into production, consequently, there remains an enormous research space to be explored emerging research materials (ERMs) that show potential for extending the feature size below sub 8 nm. Utilizing hydrophilic-hydrophobic interactions as driving force for self-assembly, we developed a method to fabricate atomic patterning platforms using different metal cation-conjugates bio amphiphiles. With this method, we were able to develop ordered line patterns with the feature size range down to 4.40±0.58 nm using Cu-conjugates bio amphiphiles. Further after solvent annealing, feature size was reduced to 0.56±0.14 nm. We demonstrate that Ni-conjugates bio amphiphiles make ordered line patterns with the feature size range down to 3.79±0.65 nm. These directed self-assembly of metal cation-conjugates bio amphiphile line patterns could serve as a cheap and effective way for manufacturing of high-resolution features, both in the semiconductor electronics industry and in high density magnetic media, enabling wide applicability in 21st century emerging technologies.
Effect of External Water in Non-Aqueous Electrolytes on the Mechanism of Mg2+ Intercalation in Tungsten Oxides

Ruocun (John) Wang, Takeshi Kobayashi, Yu Zhang, Peter V. Bonnesen, Peter Cummings, Marek Pruski, Veronica Augustyn

There is a high demand for low-cost energy storage devices with high energy density and excellent safety. Rechargeable magnesium batteries (RMBs) have the potential to achieve better performance than Li-ion batteries (LIBs) as they allow for the use of a dendrite-free Mg anode, which has about five times the volumetric capacity of the graphite anode in LIBs. One challenge for Mg-ion batteries is to improve the intercalation kinetics of oxide-based cathode materials. The addition of water in non-aqueous electrolytes has been shown to improve the kinetics of Mg2+ intercalation, but the mechanism and the effect of water concentration are still under debate. To shed light on these issues, this research focuses on a systematic addition of water into a 0.1 M Mg(ClO4)2 in acetonitrile electrolyte and its effect on Mg2+ intercalation in WO3 and WO3·H2O. Cyclic voltammetry (CV) was used to analyze the electrochemical performance. Solid-state 1H nuclear magnetic resonance spectroscopy (NMR) and inductively coupled plasma – optical emission spectrometry (ICP-OES) were used to study the intercalation mechanisms in the cathodes. Solution 1H NMR and molecular dynamic (MD) simulation were used to understand the water solvation effect in the electrolytes. An improved rate capability as a function of sweep rate and a decreased peak separation of the redox couples for both materials were found as more water was introduced to the electrolyte until the water concentration reached around 14,000 ppm. Based on these studies, we find that the most likely intercalation mechanism from these electrolytes is the co-intercalation of Mg2+ and H+. The protons were not present in the electrolyte, which means they were likely to be generated at the interface through hydrolysis. This mechanism can be general to other oxides benefitting from the addition of water into non-aqueous multivalent electrolytes.
A Comparison of Thermionic Filament and Carbon Nanotube Field Emitter Array-based Ion Sources in Coded Aperture Miniature Mass Spectrometers

Raul Vyas, Philip J. Herr, Tanouir Aloui, Kathleen Horvath, Matthew P. Kirley, Charles B. Parker, Adam D. Keil, James B. Carlson, Justin Keogh, Roger P. Sperline, M. Bonner Denton, Brian R. Stoner, Michael E. Gehm, Jeffrey T. Glass, Jason J. Amsden

This work presents a comparative study of thermionic filament and CNT emitter array-based electron sources in a cycloidal-coded aperture miniature mass spectrometer (C-CAMMS). The use of spatially coded apertures in mass spectrometry enables miniaturization by improving throughput without sacrificing resolution. To enable the full advantages of spatial aperture coding, the ion source must produce a spatially and temporally uniform sheet of ions directed at the coded aperture. Carbon nanotube (CNT)-based electron ionization sources for mass spectrometers provide several potential benefits over conventional thermionic emitters, including low voltage and power operation, room temperature operation, long lifetime, and ability to operate in a pulsed mode. In this study, electron emission stability and coded aperture image (as a measure of ion signal stability) over time were compared for C-CAMMS containing a CNT based ion source and a thermionic filament-based ion source. We found that the thermionic filament produced a much more stable coded aperture image than the CNT based ion source. The greater fluctuations in the CNT based source are a result of adsorption and desorption of molecules on the CNT surface that cause local work function changes. These work function changes lead to spatial and temporal fluctuations in the electron emission and ion signal. Possible solutions to the CNT spatial and temporal fluctuations are discussed.

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Binary MnO$_2$ and Co$_3$O$_4$ Nanostructure on Well-aligned Electrospun Carbon Nanofiber for High-performance Nonenzymatic Glucose Sensor

Ziyu Yin, Xinping Zeng, Jianjun Wei*

This work reports a highly sensitive and selective electrochemical biosensor based on well-aligned electrospun carbon nanofibers (ECNFs) bearing hybrid nanocomposites of Co3O4 and MnO2. The hybridization of Co3O4 and MnO2 nanostructures has been synthesized by a simple and economical one-step template-free electrodeposition technique with a constant low-current (60μA) for 3h, which realized the formation of a uniform binary MnO2/Co3O4 film on well-aligned ECNFs (MnO2/Co3O4@ECNFs). The nano-matrix electrode exhibits featured structural and electrochemical properties, including better uniformity, larger active surface areas, faster electron transfer, and a maximum electrooxidation towards glucose in comparison with electrodeposition of only MnO2 or Co3O4. The glucose-sensing performance of the fabricated hybrid structures was measured by cyclic voltammetry (CV) and chronoamperometry (CA). The binary MnO2/Co3O4@ECNF electrode has shown superior sensing performance including a rapid glucose response within 5 seconds, a wide range (0.005mM to 10.89 mM), excellent sensitivity of 973.91 μA mM-1 cm-2 (0.005mM ~0.57mM), and a detection limit of 0.02 μM (S/N=3) with satisfactory selectivity, great reproducibility and stability. These features indicate that as-synthesized MnO2/Co3O4 binary nanostructure decorated well-aligned ECNFs hold great potential in the development of a commercialized glucose sensor.
Interaction in MoS2- Graphene System

Sajedeh Pourianejad, Frederick Aryeetey, Olubunmi Olumide Ayodele, Shyam Aravamudhan, Tetyana Ignatova

Exciting properties of Layered materials have been led Scientists to study them further a century. While, realizing the true potential of these systems have been grabbed attention to generate advanced technological applications during these recent years. High-quality junction between semiconductor and metallic contact with no energy barrier is crucial for high-performance device, which is hard to achieve for 2D MoS2 because of its large bandgap. Heterostructure of single-layers graphene /MoS2 has been demonstrated as a promising candidate for diverse unique optoelectronic devices owing to the high transparency of graphene, the tunability of its Fermi level and the magnificent optical properties of MoS2. Transfer of graphene or other 2-d materials from their growth substrate on which have been synthesized to application substrates is of great importunate. Although the synthesis steps can have a key role on quality improvements, it is important to acknowledge that most of the time degradation of quality occurs during the transfer process because of tearing and ripping of the 2-d layers. There may be more merit in reducing the degradation during transfer than making other improvements. To ascertain the MoS2 and graphene layer number and their defects, Confocal Raman spectroscopy and photoluminescence measurements were conducted before and after transfer. To identify the thin film thickness atomic force microscopy (AFM) was performed. Scanning electron microscopy was used to investigate the surface morphologies of MoS2 and Graphene. To investigate work function and charge-related phenomena on surfaces, Kelvin probe force microscopy (KPFM) and Electrostatic force microscopy (EFM) were carried out. We speculate that the tunable Fermi level in graphene allows excellent work-function match with MoS-2, resulting in low contact resistance.

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The role of TiN as a capping layer on the ferroelectric HfO2

Younghwan Lee, H. Alex Hsain, Gregory Parsons, Jacob L. Jones

The first ferroelectricity in HfO2 was reported in 2011. Since its discovery was found accidentally, many research groups across the world have studied HfO2 material to understand the origins of the development of ferroelectricity. It is now believed that the emergence of polar phase of HfO2 (orthorhombic, space group of Pca21) generates ferroelectricity among other non-polar phases such as monoclinic and tetragonal. It has been reported that possible driving factors, such as dopants, thickness, surface energy, annealing conditions, and capping layer, can impact the development of orthorhombic phase significantly. In this study, we studied TiN via ALD and RF sputtering as a capping layer and their role on the HfO2 based thin film. TiN with different preferred-orientation of (111) and (002) was fabricated via ALD successfully. Structural and chemical characterization was done for both TiN and the electrical property was measured. In addition, the phase evolution of HfO2-ZrO2 thin film under TiN capping layer via RF sputtering is also studied.
Porosity is often desired in polymers. For most applications, the pore sizes must be small enough that bulk physical properties are retained, but significant enough to enhance mechanical properties. The objective of this research was to create spherical pores in a silicone matrix by removing the core material or filler. Silicone microspheres were developed and removed by wash techniques, as evidenced by the SEM images. Other materials like polystyrene and salt were also embedded in the polymer matrix and subsequently removed. Thermogravimetric analysis was performed on samples before and after removal of filler materials, to further determine if materials were removed. Rheology information of the polymer matrix was also collected to investigate whether the polymer with the dispersed phase can be extruded. The preliminary results look promising, and more work would be done in the future to optimize the production of silicone microspheres, as well as their distribution in and removal from the polymer matrix.
It’s Good to be Flexible: Energy Transport Facilitated by Conformational Fluctuations in Light-Harvesting Polymers

Leah M. Rader Bowers, Egle Puodziukynaite, Li Wang, Zachary A. Morseth, Kirk A. Schanze, John R. Reynolds, John M. Papanikolas

The mechanism of energy transfer between Ruthenium (II) (Ru) and Osmium (II) (Os) polypyridyl complexes affixed to a polyfluorene backbone (PFRuOs) is investigated using a combination of time-resolved emission spectroscopy and coarse-grained molecular dynamics (CG MD). Photoexcitation of a Ru chromophore initiates Dexter-style energy hopping along isoenergetic complexes followed by sensitization of a lower energy Os trap. While we can determine the total energy transfer rate within an ensemble of solvated PFRuOs from time-dependent Os emission spectra, heterogeneity of the system and inherent polymer flexibility give rise to highly multiexponential kinetics. To determine how energy transfer is influenced by conformational motion, we developed a two-part computational kinetic model to supplement our spectroscopic results: 1) CG MD model of PFRuOs that simulates molecular motions out to 800 ns and reduces computational time by ~400x compared to all atom MD and 2) Energy transfer kinetic simulations in CG MD PFRuOs that produce time-resolved Ru and Os excited state populations. Good agreement between simulated and experimental emission transients reveals our kinetic model accurately simulates the molecular motion of PFRuOs during energy transfer. Simulated results indicate that pendant flexibility largely enables high transfer efficiency. When pendants on our CG PFRuOs model keep their inherent motions, energy transfer is 80% efficient, while a 62% efficiency is achieved when pendants are treated statically.
Inhomogeneous Electric Field-induced Phase Transitions in Potassium Sodium Niobate-based Piezoceramic

Jianwei Zhao, Stephen Funni, Elizabeth Dickey, Jacob Jones

Potassium sodium niobate (KNN)-based material is one of the promising lead-free piezoceramics and has been used to fabricate multilayer ceramic actuators (MLCAs). Particularly, a KNN piezoceramic with a mixed orthorhombic/tetragonal (O/T) phase composition is preferred in an MLCA because of its high d33 coefficient. However, with an applied voltage, high electric field concentrations can develop near the interdigitated electrode edges in an MLCA and induce the O/T phase fraction changes. To probe phase transitions due to the electric field inhomogeneity, in situ high-energy X-ray diffraction (XRD) at advanced photon source (APS) was carried out on a KNN bulk sample with partial electrodes. Under the application of a bipolar electric field up to 3 kV/mm, an ultra-small X-ray beam sequentially probed a region of interest under the electrode edge, revealing inhomogeneous O/T phase fraction changes throughout the scanned pixels. Integrated with the finite element modeling (FEM) on distributions of the electric field, strain, and stress, it shows a good correlation between phase fraction changes and electric field magnitudes. The fundamental science revealed in the work will help enhance the design and reliability of MLCAs in piezoceramic devices.

This material is based upon work supported by the National Science Foundation (NSF), as part of the Center for Dielectrics and Piezoelectrics under Grant Nos. IIP-1361571 and IIP-1361503.
Systematic study of Nano-structured surface induced rupture of pathogenic fungi to define conditions for novel nano anti-fungal polymers

Naga Venkatesh Kollu, Dennis R LaJeunesse

Background: Candida albicans, a dimorphic fungus responsible for most candidiasis infections in humans mainly in immunocompromised patients such as transplant recipients and AIDS patients. Drug resistant strains of C. albicans are an enormous health concern and like most antibiotic resistant microbes pose a greater risk due the concomitant acquisition of traits associated with pathogenicity. Traditionally microbial control involves antibiotics that target specific essential enzymes; however, over the past fifty years there has been an exponential increase in resistance of pathogenic bacteria and fungi to known antibiotic compounds. Nano-structured surface (NSS) are attractive alternatives to chemical antibiotics as they are not susceptible to the same pathways towards resistance as chemical agonists. We aim to define the surface properties of these NSS materials and use these properties for the design and application of novel materials that control pathogenic fungal growth and biofilm formation.

Methods: Rupture of C. albicans and changes in cell wall composition on the NSS will be tested by a Live-Dead assay using the fluorescent dye Fun-1 and calcofluor white which stains chitin in cell wall using confocal microscopy and are confirmed using scanning electron microscope. Microcolony assay is performed to see the effect of mechanical stress on morphogenesis from yeast to hyphal forms. The relation between mechanical modulus of NSS and C. albicans and drug-resistant strains of C. albicans with be tested using Atomic force microscopy.

Results: The NSS-C. albicans interactions confirmed an increase in adhesion and chitin concentration in cell wall with the increase in time of incubation and the timing of rupture of C. albicans on NSS is confirmed as at 8 hour incubation. Nano-cones on the cicada wing inhibit the transformation of yeast to hyphae thus reducing pathogenicity. Finally, we define conditions for controlled rupture and adhesion and pathogenesis of drug resistant strains of C. albicans on NSS.

Conclusions: Although there is great potential for NSS application, there are no clearly defined limitations of NSS as a mechanical control of fungal growth, or how a cell may develop resistance; by studying the mechanism of NSS rupture, this study will also, be the first to study this aspect of NSS in any system. The mechanism behind the rupture of pathogenic fungal cells is crucial when designing anti-fungal surfaces. This study will examine the mechanical roles of the yeast cell wall in the evolution of fungal/host interactions, especially in the context of drug resistance.
Toxicity assessment of Cerium dioxide nanoparticles on the lung epithelial and endothelial cells using Co-culture model

Lakshmi P. Beeravalli, Shyam Aravamudhan, Joseph M. Starobin

Respiratory diseases due to penetration of ultra-fine particles are steadily increasing. The main portal of entries for such particles is a gas-exchange region of the lung which has the large absorption area with a thin alveolo-capillary barrier. The goal of this work is to study this barrier and investigate in-vitro toxic effects of 15-30nm nanoceria on A549 epithelial cell line and EA.hy926 endothelial cell line monocultures. We aimed to determine the cytotoxicity of nanoceria based on particle size and aggregation characteristics using membrane integrity and ROS assays. For this purpose, tween-80 was used to determine the toxicity in comparison with complete media. The A549 and EA.hy926 cell lines were cultured on either side of a permeable transwell insert to establish the co-culture and mimic the complex 3D- structure of alveolo-capillary barrier. We found that A549 cells failed to form the tight junctions necessary for forming a functional barrier in-vitro, therefore we treated them with dexamethasone. Dexamethasone helped to form the tight junctions which was confirmed by measuring electrical resistance across the barrier using TEER(Trans epithelial/endothelial electrical resistance). Our experiments demonstrated that the cerium dioxide nanoparticles in aggregated form showed a higher cellular toxicity compared to the tween-80 control experiments. We have established that our co-culture system provides a suitable in-vitro model to examine the effects of nanoparticles on the alveolo-capillary barrier and to investigate the mechanism of particulate matter toxicity across this functional barrier.
Generating Clean Fuels from Water: The Role of Surface Sites and Inter-facial Dynamics of Photocathodes

Aaron D. Taggart1, Jake M. Evans1, Lesheng Li, Katherine J. Lee, Bing Shan, Christina M. Klug, R. Morris Bullock, Jillian L. Dempsey, Thomas J. Meyer, Yosuke Kanai, and James F. Cahoon

Tandem water splitting with wide-bandgap metal oxides functionalized with chromophore-catalyst assemblies is a potential low-cost solution to synthesize solar fuels. However, many of these dye-sensitized photocathodes are based on NiO scaffolds which exhibit poor performance and limit the catalytic efficiency in aqueous conditions and at potentials needed for tandem water splitting. Here, we elucidate that in the presence of water, intra-bandgap surface states exist that are associated with hydroxyl and oxygen moieties adjacent to Ni vacancies. Through a combination of electrochemical measurements and First-principles calculations, we show that these trap states give rise to a surface capacitance which can be almost completely eliminated by targeted atomic deposition (TAD) of Al treatment. TAD-treated electrodes functionalized with chromophore-catalyst assemblies sustain cathodic photocurrent at positive electrochemical potentials and yield a champion Faradaic efficiency of 46.0 ± 5.9% for H2 evolution compared to 3.1 ± 0.4% for untreated films at +0.73 V vs. RHE. To the best of our knowledge, these results are the most positive potentials at which H2 evolution has been observed for a dye-sensitized photoelectrosynthesis cell to date, and represent an important step toward designing tandem water splitting devices with high efficiencies. In addition, progress is being made to develop new photocathode materials such as PbTiO3 which show promising ferroelectric properties that could enhance charge injection, collection, and overall efficiencies.
Doped Semiconductor Materials Properties Can Alter the Biofilm Behavior

Alexey V. Gulyuk, Dennis R. LaJeunesse, Pramod Reddy, Ronny Kirste, Ramon Collazo, Albena Ivanisevic

A treatment of GaN samples with UV light introduces alterations in surface charge and chemistry. The behavior of Pseudomonas aeruginosa films also changes in response to substrate property modification. The GaN surfaces were characterized by atomic force microscopy, Kelvin probe force microscopy, and X-ray photoelectron spectroscopy. The Pseudomonas aeruginosa film responses were quantified by measuring amount of catalase, reactive oxygen species, and intracellular Ca2+ concentrations. Performed studies support the hypothesis that certain P. aeruginosa biofilm characteristics can be tuned by the interfacial properties and the length of the biofilm-substrate interaction.
Get a Grip: Creating Soft Robotic Grippers via Self-folding by Infrared Activation

Ana Ratanaphruks, Amber Hubbard, Elton Luong, Russell Mailen, Jan Genzer, Michael Dickey

Robotic technologies have greatly expanded our ability to interact with our surroundings. In particular, soft robots can handle delicate objects without damaging them. However, they are made from materials that can be weak and require continuous exposure to stimuli in order to maintain functionalities. Self-folding grippers made from pre-strained polystyrene (PS) are an innovative way to remove these limitations because this commonly available and inexpensive thermoplastic maintains its shape and ability to hold cargo after the removal of stimulus (IR light). When IR light is absorbed in specific areas of PS, localized heating causes the polymer to reach its glass transition point where segments of the polymers are free to move resulting in out-of-plane folding. IR light is absorbed faster in areas marked with ink so with specific ink patterns, PS films can fold without manual manipulation and transform 2D patterns into 3D shapes. These grippers were studied and optimized based on geometry, ink placement & density, endurance, strength, and reproducibility. They were found to have better endurance and strength than other soft robotic grippers; these devices were capable of withstanding ~1 kg of weight for several months or withstanding 24,000 times their own mass for shorter time spans. Given the advantages of these PS grippers, they can be used for remote and autonomous tasks such as packaging and manipulating objects of various shapes and sizes as small as 0.5 cm. Self-folding PS is shown to be a novel technique in creating grippers and extending the applications of soft robotics.
Enhanced Darkfield Hyperspectral Imaging System as an Analytical Tool to Distinguish Between Monolayer, Few-layer and Multilayer MoS2

Sahil Tahiliani, Frederick Aryeetey and Dr. Shyam Aravamudhan

Transition metal dichalcogenides (TMDCs), a type of atomically thin 2-D semiconductor, have been incorporated into optoelectronics, flexible integrated devices etc. The TMDCs like molybdenum disulfide (MoS2) have numerous beneficial qualities, including being stable, non-toxic, thin, light, mechanically strong and unlike graphene, can be directly grown on insulating substrate. Also, it exhibits good optoelectronic properties and bandgap tuning by varying the thickness. In this study, an in-house setup was used for CVD-based synthesis of MoS2 film exhibiting monolayer, few-layers and multilayer flakes. Characterization of films was done by Raman and photoluminescence spectroscopy to confirm bandgap, morphology, and atomic force microscopy was used to confirm sample thickness. But there exists a need for a novel and direct analytical tool that requires minimal time and sample preparation to analyze MoS2 samples to study the layers/thickness. In that regard, this is a first report on using Enhanced Darkfield Hyperspectral imaging system that combines imaging and spectrophotometry, using advanced optics and algorithms to capture spectra from 400-1000 nm at each pixel into a datacube. This system has been used to successfully differentiate the MoS2 sample region as mono/few/multi-layers in accordance with conventional methods and serves as basis for further protocol development for other 2D materials.
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Hybrid Dielectric/Metal Nanowires for Low-loss and Deep Sub-wavelength Plasmonics

Corban Murphey, Seokhyoung Kim, James F. Cahoon

Plasmonic materials can confine and guide light on a deep sub-wavelength length scale (i.e. the material is 10x smaller than the confined wavelength) for diverse applications in sensing, catalysis, and nano-optics. However, plasmonic materials are often limited by the large Ohmic absorption losses associated with the metallic nature of the materials, resulting in undesirable heating effects and short propagation distances in waveguides. In comparison, dielectric materials have substantially lower losses than metals, but they are not able to confine light on the same deep sub-wavelength scale. This raises the question: can we engineer a hybrid plasmonic/dielectric nanostructure that confines plasmonic modes into a dielectric medium to simultaneously achieve deep confinement and low loss? Here, we show that a simple yet unexplored geometry, a core/shell dielectric/metal nanowire, will exhibit unique plasmonic modes that achieve this goal. By tuning materials and geometric parameters, we hope to develop wavelength selective waveguides.
The 21st century has presented itself as the age of information, bringing with it amounts of data existing on a scale that could only have been dreamt of fifty years ago. Machine learning has emerged in parallel with this amount of data as an excellent method of classifying and extrapolating from these large data sets. However as the datasets grow larger, their associated neural networks become more computationally expensive to train. Additionally, we are fast approaching the physical computing limits of our traditional transistor-based machines, while demand from large data sets and machine learning algorithms grows ever larger.

Neuromorphic computation, in mimicking the information processing of biological brains, has presented itself as a possible alternative to traditional computing. One method of neuromorphic computation is memristive neural networks, which utilize memristors and simulates biological synapses via their unique properties. However, methods of neuromorphic memristive computing have lacked the ability to obtain a practical intersection of high density network architecture, low power operation, and small size. Here we present a method of creating a percolating device network of DNA-wrapped carbon nanotubes (CNT) with intent to display macrological and low-voltage memristive behavior and exert nanoscale control at individual connection points of the percolating network. With further development, the molecular control over conductive materials described in this poster could be paired with neuromorphic computation methods in order to create a computing platform which more closely mimics biological brains than traditional methods.
Investigating the Role of Interlayer Water in δ-MnO2 During Electrochemical Energy Storage

Kevin Matthews, Shelby Boyd, Veronica Augustyn

δ-MnO2 (birnessite) is a layered transition metal oxide of interest for electrochemical energy storage. The interlayer of birnessite contains alkaline or alkaline earth metal cations and flexible water bound by electrostatic interactions to the manganese oxide layers. In aqueous electrolytes, we hypothesize that the interlayer water improves the energy storage kinetics. However, these water molecules can be removed under low pressure or raised temperature, both environments often experienced during electrode preparation. Because of the variability of material processing before electrochemical testing, we must investigate the stability of the interlayer water and its role in the energy storage kinetics of birnessite. To do this, we synthesized KxMnO2·yH2O (K-birnessite) via a hydrothermal method. We confirmed the synthesized material to be K-birnessite via Raman spectroscopy and X-ray diffraction (XRD). The presence of interlayer water after heat treatment was investigated using thermogravimetric analysis and in situ XRD. To study a dehydrated form of the material, non-aqueous electrochemistry was performed in an argon environment. The interlayer was monitored throughout electrode processing using ex situ XRD. The material’s electrochemical energy storage capability in aqueous and non-aqueous electrolytes was investigated using cyclic voltammetry. This study sheds light on the sensitivity of interlayer water in birnessite during common energy storage electrode processing steps, and how it affects its electrochemical energy storage performance.
Renewable nanotechnology involves the production and use of nanoparticles from renewable sources such as wood. Nanosized cellulose particles such as cellulose nanofibrils (CNFs) have an additional benefit of being sustainable, biocompatible and biodegradable in comparison to synthetic nanoparticles.

Cellulose nanofibrils are commonly produced from bleached wood pulp (i.e. without lignin) by combination of low and high-shear intensity mechanical treatments. The low-shear intensity treatments can be conducted using lab-scale refiners such as a PFI mill refiner. This low shear step initiates fiber fibrillation and reduces flocculation of pulp fibers. The high-shear intensity treatments induce more severe mechanical action on the pulp fibers, resulting in increased fiber fibrillation and dimensional reduction with subsequent dispersion of the assembled nanofibrils. However, the high-shear mechanical treatments require non-flocculated fibers as input to limit clogging and reduce the energy needed for fibrillating the materials. Recent studies have attempted to optimize the fiber fibrillation for CNF production using high-shear intensity treatments alone, but the impact of the low-shear intensity mechanical treatments remains unclear.

This work aims to understand the influence of refining on the fibrillation process of cellulose fibers for the production of CNFs. A second component of the work consists of correlating the CNF degree of fibrillation with the physical and mechanical properties of anisotropic CNF foams made by directional ice-templating. In this work softwood and hardwood Kraft market pulps were refined using a PFI mill refiner at 10K, 20K and 40K revolutions. The degree of fibrillation of the refined cellulose fibers was evaluated by water retention and cationic demand measurements. The refined fibers were then processed through an ultrafine
friction grinder (high-shear mechanical treatment), at a pre-defined specific energy consumption value of 0.5 kWh/kg to produce aqueous CNF suspensions. The porous structure and compressive strength of foams produced from the 10K, 20K and 40K CNFs were assessed by scanning electron microscopy and uniaxial compressive testing, respectively. The compressive elastic modulus of CNF foams made of hardwood decreased with increased refining whereas the modulus of the CNF foams made from softwood fibers remained relatively constant. Differences in mechanical performance of CNF foams suggest that the hardwood fibers are more susceptible to mechanical damage during PFI refining than the softwood fibers. In case of hardwood, the optimum mechanical performance of CNF foams at the initial refining intensity of 10K revolutions can be correlated to effective nanofibrillation of cellulose fibers. This work provides a potential pathway for production of CNFs with controlled degree of nanofibrillation.
X-Ray scattering techniques are valuable resources in phase identification and crystallographic structure determination. The understanding of phase information, segregation, and crystallographic changes of various material systems can be used as a basis for determining the underlying causes of interesting properties and behavior, such as ferroelectricity. Recently, progress has been made both in the execution of XRD experiments and the statistical techniques used to fit, process, and analyze the data. New, highly sensitive detectors and unique sample stage apparatuses have allowed for increased time resolution and increased capability of in situ experiments that vary applied electric field and temperature. In the analysis of the resultant data, Bayesian statistical methods have been explored to quantify the uncertainty and more thoroughly describe the parameters that give rise to measured diffraction patterns. This poster will describe the details of experiments which leverage the strength of x-ray scattering techniques and utilize Bayesian statistical methods of data analysis to study a variety of material systems of interest. The work includes an in situ x-ray study with varying temperature and applied field of the lead manganese niobate (PMN) ferroelectric material system to explain the origin of joule heating and electrocaloric fatigue behavior that was experimentally observed. Details will also be given of the use of synchrotron XRD and pair distribution function (PDF) study of the related solid solution material system of lead magnesium niobate – lead titanate (PMN-PT) to elucidate the phase-change-based origin of its ferroelectric properties and relaxor behavior. Finally, a fundamental in situ temperature varying synchrotron x-ray diffraction study of phase separation in several binary material systems that exhibit a miscibility gap and subsequent use of Bayesian statistical methods to describe the nature of the phase separation will be described.
Production of Cellulose Nanomaterials from Sunflower Stalk Wastes and Potential Applications

Ekrem DURMAZ, Saim ATEŞ, Stephen S. KELLEY, Nathalie LAVOINE

Cellulose nanomaterials (CNMs) are a general term which identifies various cellulose nanoparticles like cellulose nanofibers, cellulose nanofibrils, cellulose nanocrystals, nanocrystalline cellulose, cellulose nanowhiskers, microbial cellulose etc. and also they have been preferred mostly by comparison synthetic nanomaterials due to their renewable, biodegradable, eco-friendly properties. CNMs generally have been produced from different types of wood pulp, however in this study, we assessed the potential of sunflower stalk wastes to be converted into CNMs, namely cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) for the design of high-value added products because the cultivation potential of sunflower is high in Turkey and their wastes remained in abundant amounts can not be evaluated compared to other agricultural wastes. This study investigates routes for the production of CNCs and CNFs from sunflower stalk wastes. Sunflower stalk wastes were collected in Samsun, in Turkey. The wastes were first treated to extract the pulp by maceration using HNO3, followed by bleaching using NaClO2 to remove any non-cellulosic components. CNCs were produced from the bleached sunflower stalk pulp by acid hydrolysis, using H2SO4, while CNFs were obtained by high-shear mechanical treatment of the fibers using a supermasscolloider (MKCA6-5J, Masuko Sangyo, Japan). The chemical components of sunflower stalks were determined according to TAPPI standards as well as turbidity, zeta potential and TEM analyses were performed to determine whether the samples are nano-scale. As a result of this study, it was seen that sunflower stalk wastes can be as suitable as wood pulp with regard to raw material in the production of CNMs.

Key words: Cellulose nanomaterials, sunflower stalk wastes, cellulose nanocrystals, cellulose nanofibrils
Magnetically actuated dynamic iridescence inspired by neon tetra

Zhiren Luo, Benjamin Evans, Chih-Hao Chang

Inspired by the tropical fish neon tetra, we report a novel mechanism to achieve dynamic iridescence that can be magnetically tuned. This approach is based on the tilting of periodic photonic nanostructures, as opposite to the more common strain-induced color tuning. In this method, a periodic array of magnetic nanopillars serves as a template to guide the assembly of iron oxide nanoparticles when magnetized in a liquid environment. The periodic local fields induced by the magnetic template anchor the assembled particle columns, allowing the structure to tilt about the base when the angle of the applied field is changed. This effect emulates a microscopic “Venetian blind” and results in dynamic optical properties through structural coloration that is tunable in real time. The fabricated prototype demonstrates tunable reflectance spectra with peak wavelength shift from 528 nm to 720 nm. The magnetic actuation mechanism is reversible and has a fast response time around 0.3 s. This structure can be implemented on an arbitrary surface as dynamic camouflage, iridescent display, and tunable photonic elements, as well as in other applications such as active fluidic devices and particle manipulation.
Selective Production of Hydrogen from Formic Acid Catalysed by the Mononuclear Cationic Zinc Complexes [(L)Zn(H)]+ (L=tpy, phen, and bpy)

Elettra L. Piacentino  Kevin Parker  Prof. Dr. Thomas M. Gilbert  Prof. Dr. Richard A. J. O’Hair  Prof. Dr. Victor Ryzhov

A series of zinc-based catalysts was evaluated for their efficiency in decomposing formic acid into molecular hydrogen and carbon dioxide in the gas phase using quadrupole ion trap mass spectrometry experiments. The effectiveness of the catalysts in the series [(L)Zn(H)]+, where L=2,2’:6’,2”-terpyridine (tpy), 1,10-phenanthroline (phen) or 2,2’-bipyridine (bpy), was found to depend on the ligand used, which turned out to be fundamental in tuning the catalytic properties of the zinc complex. Specifically, [(tpy)Zn(H)]+ displayed the fastest reaction with formic acid proceeding by dehydrogenation to produce the zinc formate complex [(tpy)Zn(O2CH)]+ and H2. The catalysts [(L)Zn(H)]+ are reformed by decarboxylating the zinc formate complexes [(L)Zn(O2CH)]+ by collision-induced dissociation, which is the only reaction channel for each of the ligands used. The decarboxylation reaction was found to be reversible, since the zinc hydride complexes [(L)Zn(H)]+ react with carbon dioxide yielding the zinc formate complex. This reaction was again substantially faster for L=tpy than L=phen or bpy. The energetics and mechanisms of these processes were modelled using several levels of density functional theory (DFT) calculations. Experimental results are fully supported by the computational predictions.
Mike Rigsbee Photo Competition

**In Me the Tiger Sniffs the Rose**

Rucon Wang

*Double-octahedral layered tungsten oxide*

**TEM image of self-assembled ultrathin Cu(OH)$_2$ nanowires**

Gayani Pathiraja

*Synthesis of ultrathin copper hydroxide nanowires via Sol-gel*
Spider web like Nano-net

Sheikh Saudi

Composite nanofibers of natural and synthetic polymer loaded with different concentrations of hydrophilic drug were obtained by electrospinning technology. We found spider web like Nano-Net embedded within the mesh of sub-micron fibers. The drug is inducing such secondary spider-net structure with the diameter ranging from 30 to 70 nm.

The Matrix

James Custer

These are a dot array drilled into silicon with a 600 nm silicon oxide layer on top using Focused Ion Beam milling controlled by a nano pattern generation system.
Lakeside

Jon Meyers

This peaceful scene was created by evaporating PbI2 onto an SiO2 wafer followed up by a molecular intercalation of methylammonium iodide. Image is tilted at 52 degrees.

Nanowire Forest

Sarah Morley

Silicon nanowires (~50 nm diameter) along with one giant wire (~550 nm diameter) grown in a chemical vapor deposition system.
A Flower Cannot Blossom Without Sunshine

Taylor Teitsworth

Just like a real flower, these nanoflowers require sunlight to grow. Under illumination from a solar simulator, the energy produced by a silicon nanowire is enough to drive an oxidation or reduction reaction with metal ions in an aqueous solution to form a solid. In this image, MnOx was deposited on the tip of the nanowire stem in small petal-like flakes that grow to form a beautiful flower.

Puffer Particle

Christopher Ledford

Nitrogen atomized copper powder for electron beam melting
Asylum AFM Photo Competition

Conjunction of Topography and Current Mapping of GaAsSb Vertical Nanowires using CAFM

Priyanka Ramaswamy
*Mapping of GaAsSb Vertical Nanowires using CAFM*

Wind that Shakes the Barley

Ruoccon Wang & Wan-Yu Tsai
*Tungsten oxide electrodeposited on gold*
MoS2 Covered by Graphene

Sajedeh Pourianejad

MoS2 has been grown on SiO2/Si substrate by CVD method and Graphene which was grown by CVD on Cu transferred onto of MoS2
Prizes

AIF Best Paper

Emily Mihalko

Zhiren Luo

Student Oral 1st Prize

James Custer

Sponsored by RTNN
Student Poster 1st Prize

**Ruocun Wang**

Sponsored by AVS Mid-Atlantic($500) and Teledyne($100)

Student Poster 2nd Prize

**Mehul Parakh**
Student Poster 3\textsuperscript{rd} Prize

Kat Horvath

Sahil Tahiliani

Sponsored by Kurt J. Lesker and All Scientific

NNF Student Poster Prize

Younghwan Lee
ASM Hans Stadelmaier Memorial Award

Jon Meyer

Mike Rigsbee Memorial Photo Competition

Sarah Morley

Jon Meyer

Asylum AFM Image Competition

Sajedeh Pourianejad
CSS Survey Raffle

Sarah Morley

CSS Badge Raffle

Jianwei Zhou
Vendor Raffle

Jon Meyer

Shisir Devkota
Photo Album

Jason Luo from Optics 11 gives Workshop on soft material hardness testing

Keith gives AFM demonstration on imaging Biological materials
Thursday night mixer sponsored by RTNN and Kurt J Lesker

Phillip Strader interviewing Alex Hsain at mixer
Edwin Dickinson delivers his talk on Virtual Anatomy

Anna and Abby giving a wolfpack greeting at registration desk
Poster session

Phil and Nicole from NNF
Ruocun Wang getting ready to be judged

Ana Ratanaphruks also at the ready
Vendors keeping busy

Sherine Obare giving presentation in the afternoon session
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