Nanoscale Science and Technology
Room 206 A W - Session NS-TuA

Advanced Nanoscale Materials & Device Technologies

Moderators: Andrew Mannix, Standford University, **Taisuke Ohta**, Sandia National Laboratories

2:15pm **NS-TuA-1 Engineering at the Limits of the Nanoscale*, Farnaz Niroui,*** Massachusetts Institute of Technology **INVITED**

Next-generation devices for computing, sensing, and information processing leverage the unique properties of emerging low-dimensional materials. However, integrating these materials into functional nanosystems is challenged by their incompatibility with conventional fabrication techniques. To unlock their full potential, new heterogeneous integration platforms are essential. By combining top-down fabrication with the precision of bottom-up processes, we present strategies that overcome these limitations, enabling precise and deterministic integration of low-dimensional materials with down to sub-10 nm resolution. Through these strategies, we have developed new device platforms for energy-efficient computing, enhanced sensing, and quantum photonic technologies, which will be discussed in this talk.

2:45pm **NS-TuA-3 Theoretical Insights into Ethylene Hydroformylation on Transition Metal Heterogeneous Catalysts*, Shyam Kattel,*** University of Central Florida*; Sourav Ghoshal,* Florida A&M University

Traditional hydroformylation, an important oxo-synthesis route, is an industrial process to produce aldehydes by the reaction of synthesis gas, a mixture of CO(g) and H_2(g), with alkenes. Currently, hydroformylation represents one of the largest homogeneously catalyzed reactions in industry and is carried out using Rh and or Co-based transition metal complexes as a catalyst. However, the homogeneous nature of this reaction leads to difficulties in catalyst separation and recovery, active metal losses, metal species contamination in aldehydes, and corrosivity of catalytic solutions. The design of heterogeneous catalytic systems without sacrificing the activity and selectivity will avoid the drawbacks associated with homogeneous catalysts and be highly useful. However, a fundamental understanding of reaction mechanisms and key steps/descriptors that control the activity and selectivity of alkene hydroformylation on heterogeneous catalytic systems is limited.

Herein first-principles density functional theory (DFT) calculations were carried out to compute reaction energetics and kinetics of ethylene hydroformylation to C3 Oxygenates on (111) surface and small nanoparticles/clusters of eight face center cubic transition metals Cu, Ni, Rh, Pd, Ag, Pt, Ir, and Au. Our DFT and microkinetic simulations revealed that the metal surface model failed to capture the experimentally reported activity/selectivity trends, whereas the nanocluster model demonstrated excellent agreement with experimental results. The Rh nanoparticle showed a lower activation energy (0.87 eV) for the *CO and *C_2H_5 coupling reaction, a key reaction step for C-C coupling in hydroformylation reaction. Under experimental reaction conditions (~473 K, 1 atm), the results from microkinetic simulations illustrate that the selectivity of Rh nanoparticle for the formation of C_2H_5CHO (a C-C coupling product) is highest among all the metals studied in the present study for a temperature range of 450-900K. Thus, our results from DFT and microkinetic simulations provide atomistic insight into the reaction pathways of ethylene hydroformylation to C_2H_5CHO on transition metal catalysts and identify sites that promote the C-C coupling, a key reaction step in hydroformylation reaction. Finally, this work highlights the critical role of nanoparticle size and structure in tuning the selectivity of ethylene hydroformylation to a desired product.

3:00pm **NS-TuA-4 Van Der Waals 3D Assembly of 2D Nanomaterials for Scalable Electronics*, Joohoon Kang,*** Yonsei University, Korea

Two-dimensional (2D) nanomaterials have been received a great attention as potential building blocks for use in fundamental elements of (opto)electronic applications due to their diverse and remarkable electronic and optical properties. However, such fundamental demonstrations cannot be directly applied to practical applications because of scalable synthesis of high-quality nanomaterials and their proper assembly. In this presentation, I will demonstrate wafer-scale van der Waals assembly of 2D materials, which are exfoliated via a molecular intercalation-assisted electrochemical exfoliation method. The resulting materials with distinct electronic properties including metal, semiconductor, and insulator, can be assembled into various (opto)electronic devices such as transistors, diodes, logic gates, and photodetectors. Also, such solution-based approach further enables inkjet printing-based device fabrications without a conventional lithography.

3:15pm **NS-TuA-5 Impact of External Screening on the Valence and Core-Level Photoelectron Spectra of One-Layer WS_2*, Alex Boehm, Chris Smyth, Andrew Rakyoung Kim, Don Bethke, Tzu-Ming Lu, Jose Fonseca Vega, Jeremy Robinson, Taisuke Ohta,*** Sandia National Laboratories, USA

In a well-screened environment, transition metal dichalcogenides (TMDs) rearrange their charge carriers to screen the added charges, and reduce the electronic band gap. Consequently, when interfaced with dissimilar materials, a sheet of TMD would change its band gap adapted to its local external screening environment. Similarly, a well-screened environment stabilizes photo-holes or core-holes created in the photoemission process and, in turn, boosts the kinetic energy of photoelectrons resulting in the apparent smaller binding energy. Complication arises when determining the electronic band alignment of TMDs using photoelectron spectroscopy since the screening influences the material property of interest as well as its assessment approach concurrently. Using a sample that contains areas of suspended and gold-supported one-layer WS_2, we show how the electronic states of WS_2 under the contrasting effective or ineffective external screening environment align at the built-in junction. The photoelectron spectra point to the breakdown of rigid shifts between the valence states and core-levels with the core-levels shifting more than twice as much as the valence states. Additionally, effectively-screened WS_2 displays a valence state with a substantially larger photoemission linewidth than ineffectively-screened suspended WS_2. Altogether, our result provides key insights into how the local variation of the external screening environment creates essentially a heterojunction within a layer of WS_2.

The work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories and Base Programs and the Nanoscience Institute at the Naval Research Laboratory via the Office of Naval Research. A.R.K. acknowledges support from the U.S. Department of Energy, Office of Science, Division of Materials Sciences and Engineering (grant BES 20-017574). Samples were fabricated, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the US Department of Energy, Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly-owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

4:00pm **NS-TuA-8 III-Nitride Ferroelectrics for Low-Power Computing Devices*, Deep Jariwala,*** University of Pennsylvania

Since the demise of Dennard scaling, modern computer has largely relied on architectureal innovations such as multi-core processors and GPUs vs CPUs the address the evolving needs of computing paradigm. This above problem has been exacerbated since computing has largely evolved from arithmetic centric to data centric in the age of billions of internet-connected devices and artificial intelligence. Thus, dense and reliable data storage combined with fast and high bandwidth access in novel memory devices has become the frontier for research in modern computing hardware. In this regard there have been several advancements across a variety of technologies in the past three decades. Ferroelectric materials and devices are among the forefront of these technologies due to their low-power and fast switching abilities but suffer from integration challenges.

Therefore, in this talk, I will try to make the case of how novel III-nitride materials might present interesting avenues to overcome some of the above limitations being faced by Silicon hardware. I will start by presenting our ongoing and recent work on integration of 2D chalcogenide semiconductors emerging wurtzite structure ferroelectric nitride materials namely aluminium scandium nitride (AlScN). First, I will present on Ferroelectric Field Effect Transistors (FE-FETs) made from 2D materials when integrated with AlScN and make the case for 2D semiconductors in this application. I will then show our most recent results on scaling 2D/AlScN FE-FETs, achieving ultra-high carrier and current densities in ferroelectrically gated MoS_2 and also demonstrate negative-capacitance FETs by engineering the AlScN/dielectric/2D interface. Then, I will switch gears to introduce the ferroelectric diode (FeD) memory device and demonstrate multi-bit operation as well as compute in memory (CIM) using FeD devices made from AlScN.

4:15pm **NS-TuA-9 Chemical and Mechanical Modification of 2D Semiconductors for Electronic Devices**, ***Andrew Mannix***, Stanford University

Layered van der Waals materials, composed of discrete, atom-thin sheets, enable the deterministic assembly of heterostructures and precise placement of dopants and defects, offering a powerful route to tailor electronic and quantum properties. However, achieving scalable synthesis, controlled electronic interfaces, and low defect density remain major challenges for technological applications. This talk will highlight recent advances in overcoming these materials science barriers to enable next-generation (opto)electronic and quantum technologies based on 2D semiconductors and their heterostructures.

To accelerate chemically-tailored synthesis and compositional tuning of transition metal dichalcogenides (TMDCs) like WS_2 and WSe_2, we developed a hybrid metal-organic chemical vapor deposition process. Using solution-phase deposition of metal salt precursors and vapor-phase chalcogen delivery, this method provides high quality growth with precise doping, alloying, and growth chemistry modification [1]. Confined-space growth using this method enabled the selective formation of ferroelectric 3R-phase TMDC films on dielectrics [2], opening new possibilities for ferroelectric semiconductor devices and nonlinear optics.

Interfacing 2D semiconductors with electrodes remains a key challenge. We found that mechanical strain from top contacts, such as Ni on WS_2, can significantly enhance device performance—an often-overlooked effect [3]. For p-type WSe_2 transistors, we show that chloroform intercalation doping is a clean, reliable, and stable method to improve contact quality, even at low temperatures. These advances provide critical pathways toward scalable 2D semiconductor technologies.

[1] Z. Zhang, L. Hoang, et al., *ACS Nano* **18**, 25414 (2024).

[2] Z. Zhang, et al., *Nano Letters*, **24**, 12775 (2024).

[3] L. Hoang, et al., *Nano Letters*, **24**, 12768 (2024).

4:30pm **NS-TuA-10 Fabrication of Si Nanopillars Using Pmma Resist**, ***Kareena Guness***, *Zachary Kranefeld, T. Pan Menasuta, Basil. F Vanderbie, Thomas. E Vandervelde,* Tufts University

Poly-methyl methacrylate (PMMA) is the most commonly used e-beam resist. While it is cost effective, easily available, and offers the highest resolution among any polymeric resist, PMMA suffers from poor dry-etch resistance. For that reason, other resists like HSQ and ZEP are typically preferred. In this work, we report the fabrication of silicon nanopillars using PMMA, emphasizing on the process optimizations, particularly in reactive ion etch (RIE) chemistry, required to overcome key roadblocks. Electron beam lithography was used to write patterns in PMMA positive tone resist. To transfer the patterns to the substrate and achieve nanopillars of high-aspect ratios with smooth sides, RIE was employed with SF6 and O2. The hard mask was removed by soaking the wafer in remover-pg for several hours. The fabrication processes were characterized by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

4:45pm **NS-TuA-11 Nanoplastic Pillar Arrays for Chemical Sorption Assays**, ***Sandra Gutierrez Razo***, *Andrew Madison, Craig Copeland, Danuta Liberda-Matyja, John Pettibone, Daron Westly, Samuel Stavis,* NIST

Nanoplastic chemical sorption is of great interest and concern. Because of their scale, nanoplastic particles are difficult to detect and quantify. Many approaches involve optical microscopy and microspectroscopy, so we are fabricating pillar arrays on silicon wafers to produce novel nanoplastic standards. We spin coat low-density polyethylene (LDPE) films that are less than 100 nm thick. We then pattern the thin films using electron-beam lithography and oxygen etch. Control over pillar size, shape, and position enables useful calibrations. The arrays can also be used as substrates to study the sorption of chemicals onto LDPE. We begin with two florescent chemicals, rhodamine B, a common fluorophore, and and 4,4'-diamino-2,2'-stilbene disulfonic acid (DSD), an optical brightener added to laundry detergent. Further study of the correlation of fluorescence intensity and pillar volume will elucidate interactions of nanoplastic particles and chemical sorbents of environmental concern and technological interest.

The figure in the supplemental document shows LDPE films and pillars. (a-b, left) OPTIR spectra showing three absorption peaks consistent with LDPE at 2919, 2850, and 1456 cm-1 indicating that the composition does not change after patterning with electron-beam lithography and etching. (a, right) Optical micrograph showing nucleation sites and spherulite boundaries in an LDPE film before nanofabrication. (b, right) Optical micrograph showing features after patterning. (c) Atomic force micrograph showing pillars of similar height of approximately 76 nm and diameters varying from approximately 1000 nm to 100 nm, before chemical sorption. (d) Fluorescence micrograph of LDPE pillars after soaking in a rhodamine B solution. (e) Fluorescence micrograph of LDPE pillars after soaking in DSD solution. For both (c) and (d), the peak wavelength of fluorescence excitation is approximately 550 nm, and fluorescence emission is collected through a long-pass filter above 590 nm.

5:00pm **NS-TuA-12 Optimizing Nanocrystalline WO_3 Thin Films: The Role of Oxygen, Thickness, and Pressure in Highly Selective and Responsive NO Gas Sensing**, ***Somdatta Singh***, Indian Institute of Technology Roorkee, India; *Ravikant Adalati,* University of Mons, Belgium; *Prachi Gurawal, Raman Devi, Radhika Jain, Davinder Kaur, Ramesh Chandra,* Indian Institute of Technology Roorkee, India

WO_3 thin films have been deposited using the room temperature (RT) sputtered DC magnetron sputtering approach on n-type (100) silicon substrates at various O_2/Ar gas ratios, thicknesses, and pressure variations for NO gas detection. The structural characteristics of the film were examined using X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) confirms that all monoclinic-phase WO_3 thin films contain oxygen vacancies. The FESEM study revealed a nanocrystalline structure with a granular, porous morphology. This study discusses how the WO_3 thin film's stoichiometry affects the NO gas sensing capability. The sub-stoichiometric WO_3 thin film-based sensor improved performance in terms of high stability, selectivity, and fast response/recovery time. The sensor response (R_g/R_a) was approximately 52.53 for a 100 ppm NO concentration at 275°C, with a fast response time of about 26 sec and a recovery time of about 19 sec. WO_3 thin-film-based NO gas sensing has been evaluated across a range of operating temperatures (50–325°C) and gas concentrations (1–100 ppm), observing a change in sensor response. Additionally, the NO gas-detecting mechanism on WO_3's surface has been discussed. These results demonstrate the potential for creating high-performance, cost-effective gas sensors based on room-temperature sputtered nanocrystalline WO_3 thin films.

Keywords: WO_3; Thin films; Sputtering; Metal oxide; NO sensor.

5:15pm **NS-TuA-13 Effects of Anode Distance on Field Emitter Array Performance in Simulation**, ***Youngjin Shin***, *Kenneth Chap, Ellie Bultena, Akintunde Akinwande,* Massachusetts Institute of Technology

We present our exploration into channel electric field redistributions of field emitter arrays (FEAs) by simulating the electrostatics at various anode-to-emitter distances, L_{AE}. Silicon FEAs are cold cathode electron sources that have shown promise for high-power applications such as power switches. One of the limiting factors of FEAs as a power switch is its relatively low efficiency at lower voltages. Some of the factors that contribute to an FEA's efficiency are the on-voltage (V_{ON}=25V-30V), operating anode-to-emitter voltage (V_{AE}), and the gate leakage current. Typically, to achieve a higher efficiency (>99%), FEAs are utilized in high-voltage applications that require >10kV bias on the anode to maximize the ratio between V_{AE} and V_{ON} [1]. However, there are challenges in operating FEAs at high-voltages due to large amounts of leakage current when driving higher current densities. In prior works, it has been implied that electrons emitted at a non-vertical emission angle are collected by the gate electrode, increasing the leakage current [2]. L_{AE} has mainly been studied for its effects on space charge but have not yet discussed its impact on reducing the gate leakage current when the device is in saturation, improving the output power efficiency. In this study, we conduct electrostatic simulations in COMSOL to demonstrate how decreasing L_{AE} influences channel field redistribution to reduce leakage current at the gate aperture with flat and cusp anode geometries.

Our simulations show that changes in L_{AE} result in distinct local electric field distribution patterns along the gate aperture; at smaller L_{AE}, the electric field is mostly vertical, whereas at large L_{AE}, the non-uniform field has higher horizontal electric field components away from the center of the gate aperture. Fig.1 and Fig.2 show the electric field distributions across the gate apertures for a 3x3 FEA at V_{AE}=200V, V_{GE}=40V, and L_{AE}=2mm, 5mm, and 30mm for a flat and cusp anode, respectively. The field distribution at 30mm indicates that it is likely that a smaller proportion of electrons from the emitter are collected at the anode compared to the 2mm and 5mm configuration due to the electric field being almost entirely vertical across the entire gate aperture. The cusp anode shows the most dramatic difference between 2mm and 5mm, likely owing to its focused tip shape. Our results indicate that reducing L_{AE} increases the vertical electric field, encouraging the emitted electrons have a vertical trajectory towards the anode, preventing its collection at the gate. Future work will focus on

experimental validation of these findings and analyzing how to prevent breakdown at L_{AE}<5mm.

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