

Electronic Materials and Photonics Room Ballroom A - Session EM-ThP

Electronic Materials and Photonics Poster Session

EM-ThP-1 A Comparison between NbMoTaW Refractory High-Entropy Alloy (HEA) Thin Films Fabricated by Sputtering from a Single Pre-Alloyed Target and from Individual Elemental Targets (Co-Sputtering), *Nafisa Tabassum*, Old Dominion University

NbMoTaW refractory high-entropy alloy thin films were deposited using two separate sputtering paths: a single pre-alloyed equimolar composite target and individual Nb, Mo, Ta, and W elemental targets. While previous studies examined NbMoTaW films deposited from composite targets, the influence of deposition path on the microstructure and mechanical behavior remains insufficiently understood. In order to produce the same or similar equimolar compositions of the NbMoTaW films sputtered from the composite target, the sputtering power has to be tuned for each individual target. The sputtering pressure was varied between 0.2 and 1.25 Pa. Both deposition paths produced near-equiatom NbMoTaW films with stable BCC structure. FESEM, XRD and nanoindentation results showed similar pressure-dependent trends in grain size, crystallite size, dislocation density, lattice constant, microstrain, and hardness. The results indicate that sputtering pressure and film thickness dominate the microstructural and mechanical behavior, while deposition path mainly suggests processing flexibility.

Overall, this study shows that comparable NbMoTaW films can be produced by either path when composition is controlled. Composite-target sputtering offers simplicity and reproducibility, whereas individual-target co-sputtering provides compositional flexibility and cost-effective alloy design capability.

EM-ThP-2 Localized Dielectric Breakdown in Monoclinic HfO₂ MOS Capacitors on Non-Epitaxial 4H-SiC, *Melissa Mederos Vidal, Rodrigo Reigota César, Audrey Roberto Silva, Jacilene M. Medeiros, Renato Massaroto Beraldo, Marcos Vinicius Puydinger dos Santos, José Alexandre Diniz*, University of Campinas (UNICAMP), Brazil

A RF-sputtered HfO₂ thin film deposited on N₂+O₂ plasma-passivated non-epitaxial 4H-SiC substrate was investigated aiming to understand the dielectric breakdown behavior of MOS capacitors and its correlation with interface quality and defect-assisted transport mechanisms. The use of substrates without epilayers enables the evaluation of electrical limitations associated with bulk and interface defects, which are often less evident in optimized epitaxial structures.

Raman and FTIR analyses confirmed the formation of predominantly monoclinic HfO₂ and revealed the presence of an ultrathin interfacial oxide layer induced by plasma passivation (Fig. 1). Raman spectra showed characteristic monoclinic HfO₂ modes at ~526, 582, and 640 cm⁻¹, while FTIR measurements identified Hf-O vibrational bands together with Si-O-Si stretching modes associated with interfacial SiO₂ formation. These results indicate the formation of a chemically stable dielectric film and suggest that plasma treatment modifies the HfO₂/SiC interface.

Current-voltage measurements revealed high leakage current and a progressive current increase before dielectric failure (Fig. 2). The pre-breakdown region exhibited behavior consistent with trap-assisted conduction and trap-controlled space-charge-limited transport, suggesting the participation of defects located within the dielectric and at the HfO₂/SiC interface. Dielectric breakdown occurred at ~17 V (electric field of ~3 MV/cm). Although this value is lower than those typically reported for optimized epitaxial HfO₂/SiC systems, the devices maintained stable electrical behavior prior to catastrophic failure, without abrupt fluctuations associated with premature localized conduction paths.

Post-breakdown SEM and FIB analyses revealed highly localized dielectric failure confined to the probe contact region (Fig. 3). The damaged region exhibited severe morphological deformation, with local fusion of Al, HfO₂, and SiC caused by intense current flow during breakdown. In contrast, adjacent regions remained structurally preserved, maintaining a distinguishable dielectric layer and interface with the SiC substrate. These observations indicate that breakdown was dominated by localized electrical overstress rather than dielectric delamination or structural inhomogeneity.

The results provide insight into defect-assisted transport and localized dielectric breakdown mechanisms in HfO₂-based MOS capacitors fabricated on non-epitaxial 4H-SiC substrates. Furthermore, the preserved and smooth dielectric/SiC interface observed after breakdown suggests that the N₂+O₂

plasma passivation contributed to interface stabilization in the investigated structures.

EM-ThP-3 Expert-Feedback-Driven Autonomous Experimentation for Nanoscale Discovery, *Yongtao Liu*, Oak Ridge National Laboratory

Autonomous experimentation and self-driving laboratories are transforming scientific discovery through adaptive exploration (e.g., using Bayesian Optimization (BO)). However, most BO workflows rely on predefined scalar descriptors to guide experiment selection, limiting their ability to capture complex phenomena that resist simple scalar representation. Here, I will show our development of deep kernel pairwise learning (DKPL), an expert-feedback-driven framework that integrates human scientific intuition directly into autonomous experimentation. Rather than relying on explicit scalar objectives, our approach learns a latent utility function from expert evaluations of experimental outcomes to guide autonomous microscopy experiments. We further apply this approach to autonomous scanning probe microscopy studies of ferroelectric thin films and complex ferroelectric domain-wall structures in lead zirconate titanate and erbium manganite systems, where multidimensional polarization configurations cannot be adequately represented by conventional scalar metrics. DKPL autonomously identifies physically meaningful domain structures, prioritizes high-information measurement regions, and discovers complex domain-wall phenomena without requiring explicit physical parameterization. The results establish DKPL as a new framework for expert-guided autonomous experimentation capable of identifying complex nanoscale phenomena without explicit scalar parameterization. Acknowledgments: This research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

EM-ThP-4 Cycling-Driven Non-Monotonic TER Dynamics in HZO Ferroelectric Tunnel Junctions: Competing Wake-Up, Fatigue, and Memory-Window Collapse Mechanisms, *Alexander Blevins, Sanghyun Lee*, University of Kentucky; *M. David Henry, Samantha Jaszewski*, Sandia National Laboratories, USA

Ferroelectric tunnel junctions (FTJs) based on hafnium zirconium oxide (HZO) stacks show a promising platform for next-generation in-memory computing. The asymmetric Ta/HZO/TaN electrode stack is particularly attractive because the two metals exhibit different oxygen affinities. However, Ta readily scavenges oxygen and forms sub-stoichiometric TaO_x under electrical stress, whereas TaN remains chemically stable and functions as an diffusion barrier. This provides an accessible asymmetric interface for investigating cycling-induced evolution. Ultrathin HZO films < 10nm, demonstrate remanent polarization (Pr) values of 8–30 μC/cm² and facilitate tunneling-based ON/OFF resistance modulation, with ON/OFF ratios ranging from 5 to 30. However, the device-level mechanisms responsible for the non-monotonic tunnel electroresistance (TER) trajectory- including initial wake-up enhancement, subsequent fatigue, and memory-window collapse- continue to be significant challenges for existing predictive models.

In this work, Ta/HZO(6nm)/TaN FTJ devices were fabricated and subjected to comprehensive materials and device characterization, and all parameters were calibrated to experimentally extracted structural, interfacial, and polarization data to conduct the empirical and theoretical interpretation and modeling. The calibrated material and device model implemented in Sentaurus TCAD simulation reproduces the characteristic wake-up behavior emerging within 10²- 10⁴cycles, as well as the progressive fatigue that drives memory-window collapse under extended cycling, which agrees with experimental measurements. The resulting predictive model delineates degradation trajectories that align with endurance regimes from our experimental data from HZO-based devices.

We introduced the Two-regime saturating-exponential/power-law non-monotonic model with cycle-dependent Pr, which captures the experimentally observed wake-up and fatigue behavior in HZO FTJs. In the wake-up regime, oxygen vacancies redistribute from interfaces into the HZO bulk, progressively depinning ferroelectric domains and increasing switchable polarization. With continued cycling, a fatigue regime emerges in which irreversible trap generation at the reactive Ta/HZO interface due to cumulative TaO_x formation, which creates an asymmetric depolarizing field. This field destabilizes polarization and precipitates memory-window collapse. Interface trap densities are modeled independently to capture the disparate electrochemical behaviors of Ta and TaN. Cumulatively, our study quantitatively separates polarization- and trap-driven TER contributions and pinpoints the crossover cycle where the dominant mechanism shifts.

EM-ThP-5 Workfunction and Interface Guided Electrode Alloying for High TER and performance Metal-Ferroelectric-Metal HZO-based Tunneling Junction devices, *Chowdhury Haque, Sanghyun Lee, Alexander Blevins*, University of Kentucky; *M. David Henry, Samantha Jaszewski*, Sandia National Laboratories, USA

Metal-ferroelectric-metal (MFM) tunnel junctions based on HfZrO(HZO) have emerged as leading candidates for next-generation non-volatile memory and neuromorphic computing, yet the coupled dependence of tunneling electroresistance (TER), current density, and polarization retention on electrode work-function asymmetry remains poorly constrained by existing design frameworks. To address this gap, we present a comprehensive TCAD investigation that establishes stability-aware design rules for HZO ferroelectric tunnel junctions (FTJs) by treating electrode work functions as continuous, tunable variables and validating the model against experimental Ta/HZO/TaN and Ti/HZO/TiN devices.

After fabricating and calibrating devices, we conducted a systematic non-symmetric sweep of top and bottom electrodes' workfunction from 3.8-5.2 eV for varying HZO thickness (5-10 nm) through modeling and Sentaurus TCAD simulation in this study. Furthermore, we mapped target MFM electrodes based on workfunction and interface layers between electrodes and HZO. Each parameter point employed two solve sequences: a WRITE → READ (+/- 0.2V) sequence to extract on- (Jon) and off-current (Joff) and TER, and a 1 μs zero-bias hold to quantify polarization decay and compute the depolarization field (Edep). The model was calibrated against measured Ta/HZO/TaN and Ti/HZO/TiN stacks, reproducing Ta/HZO/TaN metrics (TER ~ <10 at 0.2-0.3 V and Jon < 1 × 10⁻³ A/cm², coercive voltage (Vc) < 1.0 V). For metrics for Ti/HZO/TiN devices, we used metrics (TER ~ 16 and on-current (Jon) ~ 1.2 × 10⁻² A/cm², coercive voltage (Vc) < 0.9 V), validating the chosen band-offset and ferroelectric parameters.

Our result indicates that ferroelectric polarization is required to meet dual stability constraints for stable polarization only when the net internal field (built-in field from electrode work-function asymmetry and the depolarization field from incomplete screening) remains below the coercive field. Since these contributions can add or subtract depending on polarization direction, both programmed and erased states are required to hold simultaneously to ensure reliable retention Ebi + Edep < Ec for programmed state and Ebi + Edep > -Ecf for erased state). Based on Pareto analysis, a narrow window where high TER and high on-current coexist can be achieved when built-in fields remain below the coercive threshold. Finally, we mapped optimal target work-function offsets with and without interlayers, offering a CMOS-compatible route to high-performance, retention-robust FTJs suitable for memory and neuromorphic applications.

EM-ThP-6 ErAs/Semiconductor Nanocomposites for 1550nm and 780nm pumped Multicolor Terahertz Emitters, *Angelique Gordon, Shreya Shrestha, Mohammad Tomal Hossain, Matthew Doty, Lars Gundlach, Xi Wang, Benjamin Jungfleisch, Joshua Zide*, University of Delaware

We present our latest results on ErAs/III-V semiconductor materials optimized for photoconductive devices operating at 1.55 μm and multicolor terahertz emitters. Terahertz (THz) technology remains a significant engineering challenge known as the "Terahertz Gap." This study addresses the need for advanced material synthesis designed to provide the performance and stability required for robust THz applications. Photoconductive switches (PCS) are key components for THz pulse generation and detection, but face challenges under 1.55 μm excitation. ErAs:InGaAs and other nanocomposites have been explored for this purpose, but their high electron concentration, driven by the Fermi level residing in the conduction band, limits dark resistivity. To overcome these limitations, we have recently demonstrated a pentanary digital alloy ErAs:([InGaBiAs]_x[InAlBiAs]_{1-x})] with incorporated nanoparticles as a suitable PCS material for telecom-wavelength usage. Molecular Beam Epitaxy (MBE) is chosen as the synthesis pathway for this alloy due to its unparalleled control over material composition. The incorporation of bismuth results in the formation of dilute bismuthides, a class of highly mismatched alloys. MBE enables the simultaneous management of strict growth constraints required for high quality bismuthides including substrate latticing matching, low growth temperatures (280°C), bismuth/arsenic ratio, and V/III stoichiometric growth. The freedom offered by the InGaAlBiAs short-period superlattice enables tunable bandgap engineering—aluminum raises the conduction band edge while bismuth, through valance band anti-crossing, maintains a bandgap suitable for 1.55 μm excitation. Introducing self-assembled ErAs nanoparticles produces sub-picosecond carrier lifetimes ensuring high temporal resolution while simultaneously pinning the Fermi level within the bandgap. The digital alloy approach combined with ErAs nanoparticles achieves both low carrier concentration, high dark resistivity,

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and stable electronic properties, enhancing the performance of THz photoconductive devices at 1.55 μm. Finally, we demonstrate our progress on the implementation of this digital alloy alongside a secondary film, ErAs:InAlAs, for multicolor THz emission. The development of Cl-ICP processes for the etching of ErAs/III-V nanocomposites provides access to the fabrication of mesa structures and the independent biasing of these dual films by orthogonal antennas. Inspired by Hybrid Terahertz emitters, this device allows for simultaneous operation at two distinct wavelengths, facilitating control over emerging THz functionalities such as elliptical polarization and advanced pulse control.

EM-ThP-7 Influence of Fluorine-Containing Surface Ligands on the Optoelectronic Behavior of NiO Thin Films, *Sanuthmi Dunuwila, Chaiwarut Santiwipharat*, University of Delaware; *Zonglun Li, Alexander A. Shestopalov*, University of Rochester; *Ujjwal K. Das, Andrew V. Teplyakov*, University of Delaware

Nickel oxide (NiO) is a transparent conductive oxide (TCO) widely used in electrochromic devices, photodetectors, gas sensors, dye-sensitized solar cells, and perovskite solar cells as a hole transport layer. NiO possesses a wide bandgap of 3.6–4.0 eV and functions as a p-type semiconductor, where Ni³⁺ species contribute to hole transport. In addition, NiO exhibits excellent chemical and thermal stability along with antiferromagnetic, electronic, and optoelectronic properties. However, using NiO as an inorganic hole transport layer (HTL) causes some challenges, such as an energy level mismatch between NiO and perovskite layers, which results in increased charge transfer barriers. Furthermore, defects at the NiO perovskite interface act as recombination centers for electron-hole pairs, reducing carrier lifetime. One successful approach found to be is surface modification of NiO with organic ligands.

In this work, gas-phase surface modification of NiO thin films using hexafluoroacetylacetone (hfacH) and acetylacetone (acacH) was investigated under vacuum conditions. The objective of this study is to understand the chemical reactivity of fluorinated and non-fluorinated β-diketones on the NiO surface and correlate these interactions with changes in the electronic and optical properties of the films. Surface treatment with acetylacetone resulted in enhanced electrical conductivity over the investigated temperature range, while hexafluoroacetylacetone treatment improved the optical transparency. Both ligands also increased the work function of NiO, indicating their potential for tuning and improving energy level alignment in optoelectronic applications.

X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were employed to investigate surface and interface chemical reactivity of NiO following ligand exposure. Ultraviolet photoelectron spectroscopy (UPS), conductivity measurements, and optical transmittance characterization were used to evaluate modifications in the electronic structure and optical behavior of the films before and after surface modification. These findings demonstrate that β-diketone surface functionalization provides an effective route for tuning the optoelectronic properties of NiO for next-generation optoelectronic and photovoltaic applications.

EM-ThP-8 Ultraviolet-C (UVC) Irradiation as Post-Treatment for Property Modification of Hydrogenated Amorphous Carbon (a-C:H) Thin Films, *Kenneth Lathrum, Jhonatan Gil Romero, Seanhee Jang*, University of Louisiana

Amorphous carbon thin films exhibit a wide range of properties, such as chemical inertness, high hardness, and tunable optical properties. They are utilized in many different devices such as micro-supercapacitors, batteries, solar cells, sensors, semiconductor devices, and nanomembranes. A key challenge in the successful development of these applications lies in the precision tuning of synthesis and modification parameters to achieve desired material properties.

In this study, hydrogenated amorphous carbon (a-C:H) thin films were prepared by plasma-enhanced chemical vapor deposition (PECVD) of a cyclohexane precursor and subjected to ultraviolet-C (UVC) irradiation with a wavelength of 255nm to tune the film's properties. The intensity of the irradiation light varied from 2.2 to 16.5 mW/cm². This wide range of irradiance of UVC light effectively altered the physical, chemical, and optical properties of a-C:H thin films.

The surface of a-C:H transformed from hydrophobic to hydrophilic under UVC irradiation. The surface became more hydrophilic with increased UV light intensity, reaching a minimum contact angle of 75.09° at the high intensity irradiation of 16.5 mW/cm². Atomic force microscopy (AFM) data showed a change in surface roughness under UVC irradiation. The surface

roughness was reduced with increased UV intensity. The surface became the smoothest with a roughness of 0.202 nm when exposed to UVC irradiation at 16.5 mW/cm².

Fourier-transform infrared (FTIR) spectra exhibited a prominent absorption band between 3000–2800 cm⁻¹, corresponding to various CH_x stretching modes. Deconvolution of this band reveals three primary components: sp³ CH₃ asymmetric stretching (ν_{as} sp³ CH₃), sp³ CH₂ asymmetric stretching (ν_{as} sp³ CH₂), and sp³ CH₂ symmetric stretching (ν_s sp³ CH₂). Additionally, low-intensity features observed at 1750–1500 cm⁻¹ are associated with C=C and C=O bonding. Following UVC irradiation, the FTIR spectral features shifted significantly. As the UV intensity increased, there was a decrease in the ν CH_x stretching modes and the appearance of C=O groups due to dehydrogenation and surface oxidation. Optical data indicated that UVC irradiation increased transparency and decreased density of the a-C:H films. The refractive index and extinction coefficient both decreased with an increase in UVC irradiance, reaching a minimum of 1.535 and 0.003, respectively, at 16.5 mW/cm². In contrast, the optical band gap broadened under UVC irradiance, reaching a maximum of 5.23 eV at the highest intensity of 16.5 mW/cm². The findings suggest that UVC post-treatment is a versatile tool for tuning the density, wettability, and optical constants of a-C:H films.

EM-ThP-9 Effect of Ge Incorporation on Ti/Al-Based Ohmic Contacts for N-Polar GaN HEMTs on SiC, *Alejandro Perez*, University of Illinois - Chicago

N-polar GaN high-electron-mobility transistors are promising for next-generation high-frequency and high-power electronics, but reproducible low-resistance ohmic contacts remain a key processing challenge. In this work, we investigate ohmic contact optimization for N-polar GaN HEMT structures grown on SiC using transfer length method structures with different pad widths and contact spacings. Traditional Ti/Al/Ni/Au metal stacks were compared with Ge-containing contact schemes to evaluate the effect of Ge incorporation on contact resistance, sheet resistance, and transfer length. Additional process variations, including different Ti/Al ratios and annealing conditions, were examined to understand their influence on contact formation and electrical reproducibility. Extracted TLM parameters were compared across 50, 100, and 200 μm pad geometries to assess consistency between layouts. These results provide practical feedback for improving ohmic contact recipes for N-polar GaN devices and support continued development of reliable wide-bandgap semiconductor fabrication processes.

EM-ThP-10 Plasma-Enhanced ALD of Ferroelectric Al_{1-x}Sc_xN Under Ultrahigh-Purity Conditions, *Gilbert B. Rayner Jr.*, *Noel O'Toole*, *Nathaniel Nelson*, Kurt J. Lesker Company; *Bangzhi Liu*, The Pennsylvania State University; *Jeffrey Shallenberger*, The Pennsylvania State University; *Gregory Muha*, *Piush Behera*, *Suraj Cheema*, Massachusetts Institute of Technology; *Blaine Johs*, Film Sense; *Nastazia Moshirfatemi*, General Technical Services, LLC; *Daniel Drury*, *Brendan M. Hanrahan*, Army Research Directorate, DEVCOM Army Research Laboratory; *Glen R. Fox*, Fox Materials Consulting, LLC; *Nicholas A. Strnad*, Army Research Directorate, DEVCOM Army Research Laboratory

Wurtzite aluminum–scandium nitride (Al_{1-x}Sc_xN) thin films are emerging materials for next-generation electronic and sensing technologies, yet achieving precise composition control and uniform deposition on complex three-dimensional structures remains a significant challenge. In this work, we report the ultrahigh-purity plasma-enhanced atomic layer deposition (PEALD) of Al_{1-x}Sc_xN using a supercycle approach that alternates AlN and ScN constituent processes. The process employs trimethylaluminum (TMA), bis(ethylcyclopentadienyl)scandium chloride [ClSc(EtCp)₂], and N₂–H₂ plasma as co-reactants at substrate temperatures between 215 and 300 °C.

A 60.3 nm–thick Al_{0.83}Sc_{0.17}N film deposited at 300 °C on a {111}–oriented Pt bottom electrode on Si (100) exhibits clear ferroelectric switching behavior. The film shows switched polarization values (2P_r) of 163 μC cm⁻² and 139 μC cm⁻² under negative and positive pulsing, coercive fields as low as of ±3.3 MV cm⁻¹, and a dielectric constant of 12.8–13.8 at 100 kHz under ±10 V.

Structural characterization reveals that films grown on {111} Pt are fully c–axis (0001) oriented, demonstrating high crystalline quality even along the sidewalls of three-dimensional features. When deposited on single-crystal GaN, Al_{0.83}Sc_{0.17}N exhibits strong in-plane and out-of-plane ordering consistent with epitaxial growth. Deposition over narrow trench structures further confirms uniform, conformal coating. Collectively, these results show that PEALD enables high-quality Al_{1-x}Sc_xN films suitable for advanced three-dimensional electronic and sensing applications.

EM-ThP-11 Multistate Stability of Ferroelectric Hzo FTJs in Gamma Radiation, *Samantha Jaszwski*, Sandia National Laboratories; *Megan Lenax*, University of Virginia, USA; *Benjamin Aronson*, University of Virginia; *Jon Ihelfeld*, University of Virginia, USA; *M. David Henry*, Sandia National Laboratories, USA

Ferroelectric (Hf,Zr)O₂-based tunnel junctions have shown significant promise as two-terminal resistive non-volatile memory (NVM) devices, exhibiting excellent area scaling capabilities and a high degree of compatibility with complementary metal-oxide-semiconductor (CMOS) technology. These devices can operate in a binary state, characterized by a high resistance state (HRS) and a low resistance state (LRS), as well as support multiple intermediate resistance states. We have demonstrated the functionality of these devices in both 5-bit and 4-bit configurations, enhancing data storage density and enabling advanced functionalities.

This work now seeks to separate effects in high gamma radiation environments while distinguishing impacts from the radiation and these other mechanisms of state disturb. Devices were tested in a ⁶⁰Co γ cell while states were read out. The results presented here demonstrate that HZO-based FTJs are tolerant to high levels of gamma irradiation and observed changes before and after irradiation are likely caused by time-dependent imprint, rather than the ionizing radiation. We also suggest that time-dependent imprint remains a major challenge in ferroelectric tunnel junctions, particularly for multistate devices, where even small state changes can severely degrade performance.

EM-ThP-12 Aromatic Thiol Self-Assembled Monolayers as Blocking Layers on Copper for Area-Selective ALD of Al₂O₃ and HfO₂, *Andrew Malder*, University of Missouri - Kansas City; *Sharmistha Bhattacharjee*, *Vamseedhara Vemuri*, *Henry Price*, Lehigh University; *Raja Bale*, *Nathan Oyler*, University of Missouri-Kansas City; *Nicholas Strandwitz*, Lehigh University; *Michelle Paquette*, University of Missouri - Kansas City

Aromatic thiols are an attractive alternative: they bind copper through the same strong covalent thiolate anchor while adding localized π–π interactions between the faces of neighboring aromatic rings, which may strengthen thermal stability. Vapor-dosed thiophenol, the simplest aromatic thiol, has been reported to withstand hundreds of cycles of a mild ALD chemistry, diethylzinc and water, at 150 °C, in a copper-thiolate layer whose π–π packing may resist precursor penetration [2]. What is not established is which structural features of an aromatic thiol govern its blocking ability. Do sterics and substituent electronic effects steer reactivity at the surface as they would in a reaction flask? Is it simply the angle of the exposed planar phenyl face?

To address this, we assembled a series of aromatic thiols on copper, varying the ring-to-anchor bridge length and the aromatic substituent systematically.

We will present blocking screening studies for ALD of hafnium oxide from tetrakis(dimethylamido)hafnium (TDMAH) and water, and of aluminum oxide from TMA and water, on monolayers drawn from this series. These two ALD chemistries span a range of conditions a blocking layer must survive: TDMAH is a bulky amido precursor, whereas TMA is small and strongly Lewis acidic.

Monolayer coverage before deposition and blocking after it are assessed by X-ray photoelectron spectroscopy (XPS). We will describe how the monolayers were prepared, how blocking is quantified from the XPS data, and what the relative blocking abilities indicate about how bridge length and substituent govern blocking on copper.

[1] Price et al., *Langmuir* 42, 21049 (2026).

[2] Shearer et al., *ACS Nano* 19, 11936 (2025).

EM-ThP-13 Bipolar Nanocomposite Semiconductors Produced by Combining Atomic Layer Deposition and Pressure-Assisted Sintering, *Benjamin Greenberg*, *Kevin Anderson*, *Alan Jacobs*, *Zoey Warecki*, *Todd Brintlinger*, *Chase Ellis*, *Joseph Prestigiacomo*, *Eric Patterson*, *Austin Cendejas*, *James Wollmershauser*, *Boris Feigelson*, U.S. Naval Research Laboratory

Photodetectors and solar cells based on bulk heterojunctions consisting of interpenetrating p-type and n-type semiconducting nanocrystalline networks have exhibited wide spectral ranges and high responsivities/efficiencies.^{1,2} The liquid-phase techniques typically used to produce these structures, however, impose restrictions on semiconductor materials selection and on heterojunction thickness, density, and conductivity, ultimately limiting photodetector dynamic range, stability, and speed. In this work, we explore an alternative synthesis approach based on four liquid-free processing steps performed in a controlled atmosphere: (1)

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a p-type semiconductor wafer is ball milled, forming a powder; (2) the powder is hydraulically pressed, forming a porous p-type particle network; (3) the network is infiltrated with a conformal coating of an n-type semiconductor via atomic layer deposition; (4) the coated network is densified via environmentally controlled pressure-assisted sintering (EC-PAS). The resultant monolithic solid, which we term a bipolar nanocomposite semiconductor (BNS), can attain thickness on the order of 1 mm and relative density greater than 99% while retaining crystalline grain size around 10 nm or smaller. Possible p-type components include highly covalent semiconductors such as Si and Ge that are difficult to produce by colloidal synthesis, and possible n-type components include metal oxides such as ZnO, Ga₂O₃, and In₂O₃. As a case study, we fabricate and characterize BNS samples consisting of p-type Si:B and n-type ZnO:Al with a thin (1–2 nm) Al₂O₃ interlayer deposited by ALD for interface passivation, dark current suppression, and prevention of a redox reaction between Si and ZnO during sintering. The Si:B is ball milled to particle diameters ranging from ~10 nm to several μm, and 48 ALD cycles (3 supercycles with a 15:1 ZnO:Al₂O₃ cycle ratio) are carried out to form ZnO:Al channels with a target width of ~20 nm. The presence of nanocrystalline ZnO and the absence of metallic Zn are confirmed by X-ray diffractometry. Nanostructural information from scanning transmission electron microscopy, electrical properties, and optical properties of the BNS samples will be presented and compared with those of other nanocomposites produced by analogous synthesis procedures, including recently reported unipolar SiO₂/ZnO:Al nanocomposites.³

1. M. Sulaman *et al.*, *ACS Appl. Mater. Interfaces* **15**, 25671 (2023)

2. M.-J. Choi *et al.*, *Adv. Sci.* **7**, 2000894 (2020)

3. Anderson *et al.*, *ACS Appl. Nano Mater.* **9**, 10725 (2026)

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