Atomic Scale Processing Mini-Symposium
Room 316 - Session AP1+EL+PS+TF-FrM

Thermal and Plasma-Enhanced ALD

Moderator: Virginia Wheeler, U.S. Naval Research Laboratory

8:15am **AP1+EL+PS+TF-FrM-1 Analyzing Plasma-Enhanced ALD of III-Nitrides via Experimental and Theoretical Studies**, *Steven Allaby, Heba Saleh, Fatih Bayansal,* ***Necmi Biyikli,*** University of Connecticut **INVITED**

Research efforts on low-temperature (T < 300 ℃) synthesis of crystalline III-nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early III-nitride growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma sources revealed highly (002) oriented polycrystalline III-nitride films on Si(100) and sapphire substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, we have achieved monocrystalline AlN, quasi-epitaxial GaN and (002) oriented InN films on sapphire substrates at a common growth temperature of 200 ℃.

The films were deposited using conventional metal-alkyl precursors (trimethylaluminum, triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2/Ar, N_2/H_2, N_2/Ar, and N_2-only) as metal precursor and nitrogen co-reactant, respectively. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and formed reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC) and optical properties of the III-nitride films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Moreover, a significant improvement of crystalline order has been observed for all binary nitride films grown on sapphire substrates, achieving or approaching epitaxial quality films. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, pressure).

To gain further insight into how different plasma mixtures and radical species affect III-nitride film quality, we have carried out density functional theory (DFT) based simulations of both metal-organic and plasma half cycles. The computational studies revealed how different adsorbed metal-organic precursor surface groups interact with hydrogen and nitrogen radicals by depicting energetically favorable reaction routes. These results are compared and correlated with the experimental observations, deciphering the critical role of hydrogen radicals.

8:45am **AP1+EL+PS+TF-FrM-3 Optical Bandgap and Thermal Stability Driven High–κ Engineering of HfAlO Dielectrics on a 200 mm ALD Platform**, ***Partha Mukhopadhyay,*** *Zuriel Caribe, Ivan Fletcher, Jim Fulford,* Tokyo Electron America, USA

This work demonstrates the tunable high–κ, optical, and thermal stability characteristics of hafnium aluminate ($Hf_xAl_{1-x}O$) thin films synthesized using a 200 mm high–volume batch atomic layer deposition (ALD) platform. Precise monolayer–level engineering of HfO_2/Al_2O_3 superlattice structures enables controlled Al incorporation, which systematically modulates the optical bandgap, dielectric constant, and electrical structure of the alloy. A key outcome is that increasing Al content systematically increases the optical bandgap of the alloy from 5.5 – 6.5 eV, accompanied by improved film density and structural uniformity, which directly influences the dielectric response and reliability of the material.

At lower Al content (~0.31), the alloy exhibits superior dielectric properties with κ > 22 and a capacitance density of 12.46 fF/μm^2, representing ~29% enhancement over HfO_2, attributed to suppressed oxygen vacancies and reduced trap density. With increasing Al composition, the widened bandgap increases barrier height, resulting in reduced leakage current and improved dielectric robustness. A higher Al fraction (~0.56) demonstrates a breakdown electric field of ~8 MV/cm, exceeding HfO_2 by over 3 MV/cm, while maintaining low leakage (~10^{-6} A/cm^2) even after 650 °C annealing. Notably, increasing Al content significantly enhances the thermal budget of the dielectric stack, stabilizing the amorphous phase and preventing dielectric degradation at elevated temperatures, while preserving relatively high κ values compared to pure Al_2O_3.

XPS analysis reveals systematic shifts of Hf4f and Al2p peaks toward higher binding energies with increasing Al concentration, indicating modified bonding characteristics and enhanced ionic contributions, consistent with bandgap widening and improved film stability. These electronic structure changes correlate with reduced surface charge transfer effects and improved dielectric integrity. Additionally, the films exhibit excellent capacitance linearity over applied voltage and stable frequency response, making them highly suitable for RF applications.

The 200 mm batch ALD platform ensures excellent uniformity, repeatability, and scalability for compositionally engineered dielectrics. Overall, this study highlights that Al–content–driven optical bandgap tuning, coupled with improved thermal stability and enhanced breakdown strength, provides a powerful route to customize high–κ behavior in HfAlO. This enables optimized performance trade–offs between capacitance density, leakage, and reliability, making HfAlO a compelling material system for advanced MIM capacitors in BEOL, RF, and memory technologies.

9:00am **AP1+EL+PS+TF-FrM-4 Atomic Layer Deposition Metal and Barrier Layers Enabling Next Generation Interconnects**, *Matthew Weimer, Sara Harris,* Forge Nano*; Thomas Moffat,* NIST-Gaithersburg*; Dane Lindblad,* Forge Nano*; Daniel Josell,* NIST-Gaithersburg*;* ***Arrelaine Dameron***[1]*,* Forge Nano

Device miniaturization continues to push the technological boundaries of manufacturing processes and integrated circuit (IC) manufacturing must keep pace to meet the design requirements for next-gen transistors. Back end of line (BOEL) fabrication poses several challenges to chip scaling: most notoriously the copper bottleneck in which thick barrier layers and resistance capacitance (RC) delays limit functional interconnect pitch to 21 nanometers [1]. To overcome this critical barrier, low resistivity, conformal metal films have been studied for hybrid metallization; decreasing interconnect resistance and reducing barrier layer thicknesses. As interconnect pitch decreases line-of-sight PVD copper barrier/seed layers experience pinch off and void formation [2]. This work explores the use of ruthenium (Ru) and lower resistivity thermal ALD iridium (Ir) thin films for copper seed layers to enable next generation interconnects. Thermal ALD Ir and Ru deposited at 250 ℃ both demonstrate conformal deposition on 10:1 aspect ratio through glass vias (TGVs) and show void free copper fill using a cyclic pulsed electrochemical deposition process. Deposited in partnership with ALD SiO2 and TiN layers, this completes a metal barrier seed solution for TSVs. As expected, the primary difference between the Ir and Ru is electrical resistivity. Seed film resistivity as deposited on TGVs was measured using four-point probe; a 10 nm Ru film measured 41 μΩ·cm and a 10 nm Ir film measured 16 μΩ·cm. Successful copper electrochemical deposition (ECD) at various ECD potentials, was completed with 10 nm of Ir with (resistivity 16 μΩ·cm) and 20 nm of Ru (resistivity 22 μΩ·cm) with the full layer stack for these film shown in Figure 1. Reduction in required layer thickness combined with improved electrical properties and demonstrated conformality can serve as crucial steps forward for advanced interconnects and BEOL architecture. Additionally, this work compares Ir film quality as deposited at 250 ℃ and 300 ℃. Ir deposited at 300 ℃ exhibits improved environmental stability when compared to 250 ℃ Ir as measured with 4-point probe after aging in atmosphere over several months. 300 ℃ Ir also shows a shortened nucleation delay, and optical constants (n and k) more closely aligned to bulk Ir values, as measured with spectroscopic ellipsometry. Ir film characterization for both temperatures including XPS, XRR, XRD and AFM is ongoing, and will be presented

9:15am **AP1+EL+PS+TF-FrM-5 Tuning the Mechanical Properties of Silica Aerogels Using Atomic Layer Deposition**, ***Victor Vogt,*** *Ali Madanchi, Katherine Rybkin, Andrés Miranda Mañón, Andrej Lenert, M.D. Thouless, Neil Dasgupta,* University of Michigan

Silica aerogels are a key material used in aerospace, catalysis, and energy applications due to their ultralow density and thermal conductivity as well as high solar transparency. Specifically, they show promise as an emerging transparent insulating material in concentrating solar thermal energy generation.[1] In our recent work we have shown that atomic layer deposition (ALD) can be used to improve the thermal stability of silica aerogels at high temperatures of up to 800 ℃.[2,3] This was attributed to the ability of ALD to conformally modify the pore structure of the aerogels and form a more thermally stable phase at the surface. However, silica aerogels also suffer from low strength and fracture toughness, restricting their

[1] **JVST Highlighted Talk**

potential applications and making practical implementation difficult due to the risk of brittle fracture in assembly or operation.

In this study, we utilize sub-nanometer ALD treatments to conformally modify silica aerogels with aspect ratios > 100,000:1. We demonstrate a monotonic increase in stiffness with increasing number of ALD cycles, resulting in a ~30-fold increase in elastic modulus after 3 cycles of Al_2O_3 (nominal ~4 Å thickness). This result is investigated using finite element modeling (FEM) of the aerogel nanostructure, which reveals the key factors which drive the large increase in elastic modulus. Furthermore, we show that ALD increases the fracture toughness of the aerogels, resulting in a ~7-fold increase in fracture toughness after 3 ALD cycles. Due to the ultra-thin and conformal nature of the ALD layer, the porous nanostructure is maintained, allowing the aerogels to maintain high solar transparency and low thermal conductivity. This method enables a pathway to broader applications for silica aerogels through improving their mechanical durability while maintaining the favorable properties of low thermal conductivity and high optical transparency over a range of operating temperatures.

References:

[1] McEnaney, K., Weinstein, L., Kraemer, D., Ghasemi, H. & Chen, G. Aerogel-based solar thermal receivers. *Nano Energy* **40**, 180–186 (2017).

[2] A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **33** (14), 5572-5583 (2021).

[3] Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **32**, 2108774 (2022).

9:30am **AP1+EL+PS+TF-FrM-6 Multilayer FUV Coatings Using ALD-Grown LaF_3 and ZrF_4**, ***John Hennessy***, Jet Propulsion Laboratory

We report on the targeted development of atomic layer deposition processes for high-refractive-index metal fluorides, specifically focusing on lanthanum fluoride and zirconium fluoride. The primary objective is to integrate these ALD-deposited materials into multilayer optical coatings designed for demanding far-ultraviolet (FUV) applications. By successfully combining ALD processes for lanthanum and zirconium fluorides with established processes for lower-index materials, we enable the fabrication of specialized optical components that are critical to various NASA applications. As a demonstration of this ALD capability, a 16-layer AlF_3/LaF_3 mirror was fabricated and shown to achieve an average reflectance exceeding 90% within a band centered around 140 nm. Finally, we discuss the prospects for increasing coating complexity and further optimizing FUV performance.

9:45am **AP1+EL+PS+TF-FrM-7 Controlling the Crystallinity of V_2O_5 Deposited by Plasma-Enhanced Atomic Layer Deposition**, ***Scott Walton***, *Peter Litwin, Neeraj Nepal, Maria Sales, David Boris, Michael Johnson, Mackenzie Meyer, Virginia Wheeler,* Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach to ALD generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. Importantly, by carefully controlling the plasma properties, it has been shown that the degree of crystallinity and phase selection is possible.

In this work, we demonstrate the ability to manage the crystallinity of V_2O_5 through careful control of the plasma characteristics during growth in a Kurt J. Lesker 150 LX PEALD system. We employ both plasma diagnostics and material characterization techniques to understand the process-to-structure-property relationship while varying the input power, operating pressure, and gas flow ratio. Optical emission spectroscopy (OES) and Langmuir probe measurements are used to characterize the production and delivery of energetic and reactive species to the growing film surface, while x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are used to characterize the physico-chemical properties of the V_2O_5 films. We find that by varying the operating pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline state. We link the transition from amorphous to crystalline material to the energy flux density delivered to the material surface during deposition and derive an estimate of the critical energy flux density necessary for crystallization. Lastly, we discuss these results more broadly and the applicability of these findings to other material systems. This work is supported by the Naval Research Laboratory base program.

10:00am **AP1+EL+PS+TF-FrM-8 Epitaxial Growth of VN on Si_3N_4(0001)/Si(111) Using Molecular Beam Epitaxy**, ***Nuri Oncel***, *Mehmet Ozdogan, Carlos Munoz, Deniz Cakir,* University of North Dakota*; Randy Duma,* Quantum Design*; Rajendra Dulal,* University of North Dakota

We report on the epitaxial growth of VN thin films on β-Si_3N_4 (0001)/Si(111) substrates using molecular beam epitaxy. The growth process and resulting film properties were systematically investigated using in-situ reflection high-energy electron diffraction (RHEED) and ex-situ scanning/transmission electron microscopy (S/TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive spectroscopy (EDS), and electrical transport measurements. RHEED and cross-sectional TEM analyses confirm the formation of epitaxial VN(111) films, with growth proceeding via a Volmer–Weber Island mechanism followed by coalescence. Increasing nitrogen flux during deposition significantly improves film continuity, stoichiometry, and crystalline quality. Structural characterization reveals an azimuthally aligned epitaxial relationship without the expected in-plane rotational reconstruction, indicating that interfacial bonding and strain relaxation dominate over simple lattice-mismatch considerations. XPS and EDS measurements confirm near-stoichiometric VN composition with reduced oxygen incorporation at higher nitrogen flux. Electrical measurements demonstrate ohmic transport across the VN/Si_3N_4/Si heterostructure, suggesting efficient carrier transport through the ultrathin dielectric layer via tunneling or defect-assisted conduction. Low-temperature transport measurements reveal a suppressed superconducting transition temperature relative to bulk and oxide-supported VN films, attributed to compressive strain and structural disorder. These results establish Si3N4(0001)/Si(111) as a viable platform for integrating epitaxial VN with semiconductor technology and provide insight into nitride–nitride heteroepitaxy and interface-driven property modulation.

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