Thin Films
Room 321 - Session TF+AP+EUV-FrM

Atomic Scale Patterning and Processing

Moderators: Jessica Jones, Argonne National Laboratory, **Mark Losego**, Georgia Institute of Technology

8:15am **TF+AP+EUV-FrM-1 Expanding the Library of Mask Materials for Selective Area Growth by Molecular Beam Epitaxy**, ***Corey White***, *Subhashree Seth, Daniela Montes, Daniel Bernstein,* Tufts University*; Cornell Horne Jr.,* University of Illinois Urbana-Champaign*; Minjoo Larry Lee,* University of Illinois at Urbana Champaign

Selective area growth (SAG) enables laterally structured semiconductor growth as well as seamless encapsulation of foreign mask materials and, thus, presents an appealing approach to the monolithic integration of dissimilar materials. During SAG, III-V growth is carried out at relatively high substrate temperatures and slow growth rates to mitigate the formation of deleterious polycrystalline material on the patterned mask.[1] Historically, SiO_2 and Si_3N_4 have reigned as the most prevalent mask materials for SAG by molecular beam epitaxy (MBE).[2] However, successfully utilizing new mask materials with unique properties could unlock new applications and functionalities for hybrid structures.Here, we first elucidate the properties of mask materials that determine their suitability for SAG. By comparing SiO_2 masks synthesized by different thin film deposition methods, we find that differences in SiO_2 surface roughness, stoichiometry/density, and hydrocarbon contamination all impact the adsorption of group-III adatoms during epitaxial growth. Demystifying the relationship between mask material properties and the propensity of group-III adatoms to nucleate on the mask during epitaxy not only lays the foundation to achieve SAG under less stringent growth conditions over optimized masks and predict the effects of tool-to-tool variation, but also enables the identification of new, untested mask materials that may also be suitable for SAG.Thus, in this work, we showcase complete selectivity for GaAs growth over ZrO_2 and HfO_2 masks for the first time.[3] This is achieved at approximately half of the group-III flux that can be employed for growth over SiO_2 with near-perfect selectivity due to differences in adatom desorption probabilities. Faceting of GaAs grown selectively within ZrO_2 gratings is found to be consistent with nominally identical growth within SiO_2 gratings. Namely, the facets that emerge depend wholly on crystallographic orientation of the dielectric mask patterns with growth within [010]-aligned structures being especially well-suited for epitaxial lateral overgrowth. III-V SAG over ZrO_2 and HfO_2 has applications in on-chip integration of passive and active optical components anddeterministic growth of three-dimensional ferroelectric devices, but also demonstrates the exciting potential of further expanding the palette of available mask materials. Further work integrating other novel dielectric and two-dimensional mask materials will be presented at the conference.[1]F. E. Allegretti and T. Nishinaga, *J. Cryst. Growth* (1995).[2]D. J. Ironside et al., *Prog. Quant. Electron.* (2021).[3]R. C. White and M. L. Lee, *J. Vac. Sci. Technol. A* (2026).

8:30am **TF+AP+EUV-FrM-2 Hybrid Molecular Layer Deposition of Tin-Aminates Toward EUV Resists**, ***Alex Persson***, *Long Than, Stacey Bent,* Stanford University

The leading edge of today's semiconductor manufacturing technology relies on extreme ultraviolet (EUV) lithography, utilizing a short 13.5 nm wavelength – a roughly fourteenfold reduction from the 193 nm ArF sources of previous deep ultraviolet (DUV) lithographic technologies. Use of this wavelength has dramatically reduced achievable critical dimensions, with new high-NA EUV tools resolving half-pitches as fine as 8 nm. However, the development of photoresists capable of translating this resolution into reliably patterned features has not kept pace with the breakthroughs in EUV exposure tools, making this material challenge a bottleneck to continued semiconductor scaling.

Conventional organic resists absorb EUV photons inefficiently, compounding stochastic failures at the ultrathin film thicknesses that pitch scaling now demands. The present work incorporates tin in an organometallic resist to address the need for better absorption, while amine organic linkers enable a tunable solubility switch using a metal-aminate bonding motif not yet reported in such resists. Hybrid molecular layer deposition (MLD) is used to deposit this Sn-aminate material one molecular layer at a time through alternating, self-limiting surface reactions between chemical precursors. This vapor-phase deposition technique affords molecular-level control over film thickness and structure, providing smooth and conformal ultrathin films while avoiding the challenges of solvent processing.

This presentation will introduce hybrid MLD procedures for depositing Sn-aminates as a new set of materials using tetrakis(dimethylamino)tin as a tin precursor with ethylenediamine and p-phenylenediamine as amine linkers. The stability of these materials in air and in various developers is reported, providing insight into their solubility switch mechanism and lithographic process optimization. Electron-beam lithography (EBL) is employed as an EUV proxy, and initial results indicate that Sn-aminates act as promising positive-tone e-beam resists in various developers, including HCl, KOH, and TMAH. The effect of deposition temperature on film structure, composition, stability and EBL patterning quality is discussed between 70 °C and 150 °C. Lower temperatures led to higher growth rates and higher organic content in the films, and accelerated film oxidation and decomposition in air. Optimal patterning was found with films deposited at 90 °C using ethylenediamine as the organic linker and developed in 0.02 M KOH, resulting in a dose-to-clear of 12 mC/cm^2 with a full-pitch of 25 nm. The effect of air-aging and post-exposure baking is also discussed.

8:45am **TF+AP+EUV-FrM-3 A Multivariate Approach Based on Residual Gas Analysis for Understanding Model Photoresist Processes Occurring During Exposure**, ***Muhammad Ramzan***, University of Mississippi, Pakistan*; Markus Langner,* University of Mississippi, Germany*; Kas Andrle, Meng Zhang, Bernhard Lüttgenau,* Lawrence Berkeley National Laboratory (LBNL)*; Won-Il Lee, Md Istiaque Chowdhury, Xinpei Wu,* Brookhaven National Laboratory*; Melinda Lin,* Stony Brook University*; Nikhil Tiwale, Qin Wu, Qi Zhang, Cheng Wang, Ricardo Ruiz, Michael D. Connolly, Oleg Kostko,* Lawrence Berkeley National Laboratory (LBNL)*; Chang-Yong Nam,* Stony Brook University/Brookhaven National Laboratory*; Michael J. Eller,* University of Mississippi

Photoresist processes such as photon absorption, electron generation, bond cleavage, crosslinking, and volatile-product formation are key challenges in extreme ultraviolet lithography (EUVL) that need to be understood and resolved. Here, we investigate functional-group-dependent EUV exposure chemistry using simultaneous total electron yield (TEY) and residual gas analysis (RGA) measurements on a library of model polymer photoresists with defined repeat-unit structures, including methacrylate, acid-functional methacrylate, hydroxyl-containing methacrylate, ether, aromatic, heteroaromatic, imide-containing, chemically amplified epoxy, and metal-oxide-infiltrated polymer systems. Principal component analysis (PCA) was applied to the mass spectrometry data from the RGA as an unsupervised dimensionality reduction technique. Firstly, PCA clearly differentiated between low- and high-outgassing photoresists, with high-outgassing photoresists driving the maximum variance in PC1 (24.5 %). Characteristic signals from the PC loading plots were identified and assigned to corresponding photoresists. Two fragment ions, m/z 31 (CH_3O^+) and m/z 45 ($C_2H_5O^+$), were observed during the exposure of polyethylene glycol (PEG) and poly(2-hydroxyethyl methacrylate) (PHEMA). Despite having identical mass-to-charge ratios, they exhibited opposite trends with respect to exposure dose. PEG displayed increasing intensity, whereas PHEMA showed a decrease with increasing exposure dose. This trend was attributed to differences in the scission mechanisms, with PEG undergoing a solubility switch via main-chain scission, while PHEMA undergoes side-chain scission. This allows us to distinguish these two mechanisms by the time-dependent response of characteristic fragment species. We also examined the relationship between TEY and various outgassing species and found that m/z 44, assigned to CO_2, showed a positive correlation (R^2=0.99) with TEY in metal-oxide-infiltrated polymer systems, whereas no correlation was observed in PMMA-only resists. Showing that these infiltrated resists exhibit improved electron production and increased outgassing, both of which are critical to improving resist sensitivity. Moving forward, we anticipate our approach will be extremely useful for screening unknown resists and identifying their mechanisms.

9:00am **TF+AP+EUV-FrM-4 A Single Amine Additive as Both Catalyst and Inhibitor for Area-Selective SiO_2 ALD**, ***Jeong-Min Lee***, *Stacey Bent,* Stanford University

Driven by the demand for atomic-scale precision patterning in advanced semiconductor processing, area-selective atomic layer deposition (AS-ALD) has emerged as a paradigm-shifting technique in nanofabrication, leveraging its bottom-up nature to enable spatially selective and precise film growth. In this work, we report a methodology for achieving accelerated deposition of SiO_2 thin films on SiO_2 surfaces while suppressing growth on metal oxide surfaces using a single additive molecule that acts as both catalyst and inhibitor. To overcome the limited selectivity of

conventional SiO_2 AS-ALD processes associated with the use of strong oxidizing agents, we introduce a catalytic SiO_2 ALD process. This process employs a Lewis-base catalyst that both promotes SiO_2 growth with H_2O as a mild reactant at temperatures as low as 100°C, and simultaneously inhibits growth on metal oxide surfaces such as Al_2O_3, TiO_2, RuO_x, and CuO_x. Results show that the catalyzed ALD process using amine additives exhibits a mild inherent growth suppression on metal oxide surfaces—but not on SiO_2—suggesting that interactions between the Lewis-base catalyst and metal oxide surfaces during co-injection with the precursor contribute to the retardation of SiO_2 growth. To further enhance the selectivity between SiO_2 and metal oxide substrates, an amine pretreatment was performed prior to ALD to amplify the blocking capability of the same amines as inhibitors. Comparative evaluation of pyridine and triethylamine revealed different inhibition behaviors depending on the underlying metal oxide surface, with triethylamine providing more effective growth inhibition on Al_2O_3 and TiO_2 surfaces than did pyridine. By combining the inherent growth suppression of the catalyzed ALD process with the additional blocking effect of amine pretreatment, enhanced selectivity for SiO_2 deposition on an SiO_2 growth surface and several metal oxide nongrowth surfaces was achieved. This work provides a new strategy for broadening the applicability of SiO_2 AS-ALD by leveraging the dual functionality of amine additives for both catalytic growth and surface inhibition.

9:15am **TF+AP+EUV-FrM-5 Ultrasonic Level Sensing for ALD Precursors Through the Ampoule Wall**, ***Paul Dreher***, Inficon, Liechtenstein

Precursor inventory is one of the least directly observed state variables in an ALD delivery system. It is normally inferred from run time, wafer count or recipe demand rather than measured, so the estimate drifts over the life of the source and anomalous draw down remains invisible. Where sensing is fitted it usually detects liquid presence at a few fixed heights using an element immersed in the precursor, which quantises the reading and adds a wetted surface to a corrosive high purity path.

We determine remaining liquid height from outside a stainless steel ampoule by ultrasonic pulse echo. A piezoelectric element coupled to the outer face of the vessel base launches a longitudinal pulse through the wall. The acoustic impedance contrast between steel and a typical precursor is large, so most energy is reflected at the wall, but the transmitted fraction is sufficient to produce a resolvable echo from the liquid vapor interface. The vessel wall itself becomes part of the acoustic path and no feedthrough or wetted surface is introduced.

Extracting height is an underdetermined inverse problem. The echo delay gives the product of propagation velocity and path length, while the quantity of interest is the path length alone. Sound velocity in these liquids is strongly temperature dependent with a coefficient specific to each chemistry, and ampoules operate at temperatures up to 200 C, so a calibration taken at room temperature does not transfer. The chemistry itself may also be unknown to the operator. We show that the velocity can be recovered in situ at operating temperature from the same acquisition, so height is determined with no prior property data for the fluid.

Silicone oil was used as a deliberately unfavorable test case: attenuation is high, the surface echo is correspondingly weak and higher order reverberations within the liquid produce competing arrivals that must be separated. Recovered height agrees with an independent reference to approximately 1 mm with R2 = 0.997, continuously across the full range rather than at discrete heights, and the residual is limited by the reference rather than by the sensing geometry. The result is stable from room temperature to 150 C and reproducible through repeated thermal cycles, with time of flight tracking the velocity change through heating and cooling.

Because the velocity determination responds to the liquid itself rather than to its height, it is also sensitive to changes in composition, suggesting that a single acquisition may report precursor condition alongside inventory.

9:30am **TF+AP+EUV-FrM-6 ALD-Enabled Ag/ZnO Nanostructured PTFE Membranes as Flexible SERS Substrates for Trace Molecular Detection**, ***Halil AKYILDIZ***, *Sumeyye DILER INAN, Burak SOZEN,* Bursa Uludag University, Turkey

Surface-enhanced Raman scattering (SERS) is widely used for sensitive and label-free detection of molecules, with signal enhancement mainly arising from localized plasmonic effects associated with metallic nanostructures. In this study, we developed a flexible SERS substrate by combining atomic layer deposition (ALD) of ZnO with Ag nanoparticles formed on porous polytetrafluoroethylene (PTFE) membranes. PTFE membranes were first coated with ZnO by ALD, followed by the formation of Ag nanoparticles from a silver acetate solution using UV-assisted photodeposition. The SERS performance of the prepared substrates was evaluated using crystal violet (CV) as a model analyte. CV solutions ranging from 10^{-3} to 10^{-8} M were deposited onto the substrates and analyzed by confocal Raman microscopy using a 532 nm excitation laser. The Ag/ZnO-coated PTFE membranes showed a clear SERS response to CV. Characteristic Raman bands at 732, 761, 809, 1175, 1373, 1538, 1588, and 1618 cm^{-1} were observed, and their intensities decreased as the CV concentration was reduced. The characteristic bands could still be clearly identified at a CV concentration of 10^{-7} M, whereas they were no longer distinguishable at 10^{-8} M. The intensity of the characteristic band at 1175 cm^{-1} also showed a clear dependence on CV concentration. The results show that ALD-grown ZnO can be used as an intermediate surface layer for preparing Ag-containing SERS-active PTFE membranes. Combining the flexibility and porous structure of PTFE with ALD surface modification and Ag photodeposition offers a practical approach to producing flexible SERS substrates. The prepared membranes were able to detect CV at concentrations as low as 10^{-7} M and may provide a useful platform for further development of flexible Raman-based chemical sensors.

9:45am **TF+AP+EUV-FrM-7 Low Temperature PEALD of Epitaxial AlN on GaN, Ga_2O_3, and Al_2O_3 Surfaces**, ***Jeffrey Woodward***[1], *David Boris, Michael Johnson, Daniel Pennachio,* U.S. Naval Research Laboratory*; Henry Chuang,* Naval Research Enterprise Internship Program*; Michael Mathews, Emma Rocco, Katie Gann, Benjamin Sekely, Tatyana Feygelson, Jonathan Levine-Miles,* U.S. Naval Research Laboratory*; Jennifer Hite,* University of Florida*; Michael Mastro, Virginia Wheeler, Scott Walton,* U.S. Naval Research Laboratory

AlN is a wide-bandgap semiconductor with exceptional thermal conductivity, temperature stability, and piezoelectric properties, making it a promising material for high power electronics and deep ultraviolet optoelectronics in extreme environments. While plasma-enhanced atomic layer deposition (PEALD) of AlN is well-established as a promising back-end-of-line compatible process for passivation, electrical insulation, and thermal management in devices, it typically results in amorphous or polycrystalline films, which have inferior electrical and thermal properties as well as reduced chemical resistances compared to epitaxial AlN. Most reports of epitaxial AlN growth by PEALD involve the use of atomic layer annealing (ALA), in which an Ar plasma exposure is incorporated into each cycle to induce crystallization of the surface.[1] While the effectiveness of ALA is proven, its use also increases cycle duration, which significantly prolongs total process time and can promote impurity incorporation. For these reasons, the growth of epitaxial AlN without ALA is desirable, though this is challenged by the complexity of controlling the plasma properties to achieve suitable growth conditions.

In this work, we demonstrate the growth of 30-50 nm thick epitaxial AlN films on Al_2O_3, GaN, and Ga_2O_3 at 300 °C using PEALD without ALA or thermal annealing. Plasma diagnostics were used to identify favorable conditions which produce ion energy and flux characteristics comparable to those of plasmas used in ALA. The films were characterized using x-ray reflectivity (XRR), high resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and optical measurements. The growth per cycle (GPC) and density ranged from 0.90–1.03 Å and 2.998–3.173 g/cm^3, respectively, with deposition on GaN resulting in the highest GPC and density. The topography of the films closely replicated that of the underlying material with roughness from 0.25–1 nm by AFM and 0.83–2 nm by XRR, indicating that the deposition was highly conformal. The epitaxial nature of the AlN (i.e., exhibiting a highly ordered crystalline structure with well-defined orientational relationship to the substrate) is confirmed by HRXRD and IP-GID, which show a single orientation with distinct 6-fold azimuthal rotational symmetry. While the AlN films on Al_2O_3 and Ga_2O_3 exhibit significant mosaicity, the AlN films on GaN exhibit low tilt disorder, as evidenced by narrow out-of-plane rocking curves with FWHM= 0.149 degrees (537 arcseconds).

[1] H. Y. Shih et al., Sci. Rep. **7**, 39717 (2017)

10:00am **TF+AP+EUV-FrM-8 Kinetic Stabilization of Highly Dispersed Rh on MoO_3-Modified Anatase TiO_2(101)**, ***Sineth Premarathna***, University of Washington*; Zbynek Novotny,* Pacific Northwest National Laboratory*; Charles T. Campbell,* University of Washington*; Zdenek Dohnalek,* Pacific Northwest National Laboratory

Developing approaches to stabilize highly dispersed metals on oxide supports represents one of the grand challenges in catalysis. In this context, the (101) surface of TiO_2 anatase is particularly challenging because it lacks

[1] **JVST Highlighted Talk**

surface defects and has a high propensity for metal clustering. We investigate the role of MoO_3 monomeric clusters, pre-deposited on TiO_2(101), in suppressing clustering of adsorbed Rh, using combined scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Rh deposited directly on bare TiO_2(101) sinters readily at 300 K, forming nm-sized Rh clusters with apparent heights of 3 Å and larger, serving as a reference system. When Rh is instead deposited on a (2×1)-ordered MoO_3/anatase(101) surface at 163 K, STM reveals significantly smaller, highly dispersed Rh species, with apparent heights of 1.8 Å, which remain stable to 450 K. These species exhibit a higher Rh 3d binding energy of 307.8 eV as compared to 307.2 eV of metallic Rh. Only after annealing to 600 K is significant ripening observed, and the cluster sizes approach those observed for Rh on bare TiO_2(101), while the Rh 3d peak shifts toward lower binding energy. The correlated STM and XPS evolution is consistent with increased final-state screening in Rh 3d peak as Rh clusters grow. Our results indicate that modification with MoO_3, combined with low-temperature deposition, kinetically traps and stabilizes highly dispersed Rh species. Ongoing work aims to identify the Mo-O-Rh binding motifs responsible for this stabilization and to determine whether they can stabilize isolated Rh atoms.

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