Emerging Materials
Room Regency Ballroom A-C - Session EM-WeM

EUV Litho Materials

Moderator: Ms. Haripin Chandra, EMD Electronics, USA

10:45am **EM-WeM-12 Novel Organic-Inorganic Hybrid Thin Films Deposited by Molecular Atomic Layer Deposition (MALD) for EUV Resist Applications***, **Jiyoung Kim**,* University of Texas at Dallas **INVITED**

Continued extreme downscaling of semiconductor devices and their high-volume manufacturing hinge on EUV lithography (λ=13.5 nm, EUVL), especially the soon-planned implementation of high numerical aperture (NA) EUVL. Photoresist (PR) materials are a crucial area that demands significant improvement for the high NA EUVL, particularly in achieving ultrathin thickness, uniform composition and high patterning performance (e.g., EUV sensitivity, pattern resolution, critical dimension uniformity), as well as increased etch resistance.

In this talk, we will introduce an innovative synthesis route for organic-inorganic hybrid photoresists, which leverages the molecular atomic layer deposition (MALD) of ultrathin films comprised of organic and inorganic components. Specifically, we will discuss the fabrication of a hybrid resist system, which is composed of trimethylaluminum (TMA) and hydroquinone (HQ), and its characteristics under exposure using a low energy electron beam to mimic expensive and rare EUV lithography. Most importantly, we will focus on the low-energy electron exposure characteristics, investigated using an *in-situ* infrared spectroscopy system. The TMA-HQ hybrid resists not only exhibited a comparable 100 kV EBL performance to that of HSQ (hydrogen silsesquioxane), a commercial negative-tone EBL resist but also sustained the negative tone under low-energy electron exposures down to ~100 eV and lower electron energy (evaluated in diluted AZ 300 MIF solution). Furthermore, the dose-dependent characteristics of the MALD hybrid resists were also investigated at various low electron energies via EBL and electron flood gun system. The post-development remaining thickness of the exposure dose matrices was determined using atomic force microscopy (AFM), in which the required dose to maintain 50% of resist thickness (critical dose) was estimated to be approximately 8.4 mC/cm^2 at 100 eV. The obtained *in-situ* IR absorbance spectra suggested that chemical reactions involving aromatic rings of HQ as well as the reduction of C–O bonding are contributed to the formation of a crosslinking network within the TMA-HQ hybrid resist. We will also briefly go over the dry etching characteristics of the resist, identifying a potential process window for dry development.

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11:15am **EM-WeM-14 Inorganic Cluster Synthesis and Characterization via Atomically Precise ALD in Polymers***, T. Kunene, **Alex Martinson**,* Argonne National Laboratory

Precision inorganic clusters, with atom-count between single-atom-sites and nanoparticles, offer an enticing complement of atom-efficiency, unique composition and structure that may defy bulk extended solids, and a total atom count that allows affordable first-principles computation of structure-function relationships. In previous work we demonstrated a novel route to few-atom inorganic cluster synthesis in a polymer matrix [ACS Nano 2020, 14, 11, 14846–14860] through sequential infiltration synthesis (SIS) of inorganic solids in analogy to atomic layer deposition (ALD) but that occurs within (vs upon) a soft material template. Careful control of synthesis conditions affords few-atom clusters of indium oxyhydroxide with relatively uniform structure. In more recent work, we probe the unique optical and vibrational properties of these small InOxHy clusters and begin to consider their potential for CO2 capture and conversion. We describe a refinement of the SIS process that favors the formation of new clusters in the first cycle, while favoring cluster growth only in subsequent cycles. This approach affords more uniform cluster growth with characteristic vibrational spectra as acquired with in situ infrared spectroscopy. Spectral analysis provides insight into cluster size and chemical functionality that evolves with additional SIS cycles (i.e. cluster growth). Optical absorption spectroscopy further reveals the unique and size-dependent properties of the few-atom clusters relative to bulk phases. Gentle thermal treatment of the polymer-embedded clusters provides the first insight into SIS-derived cluster stability, which exceeds 200 °C.

11:30am **EM-WeM-15 Molecular Layer Deposition of Al- and Hf-Based Hybrid Resists for Electron-Beam and EUV Lithography***, A. Ravi, J. Shi, J. Lewis, **Stacey Bent**,* Stanford University

The development of new resist materials is required to enable extreme ultraviolet (EUV) lithography for next-generation microelectronics. Inorganic resists are a promising class of materials because compared to traditional organic resists, they have higher etch resistance, are more impervious to pattern collapse, and are more absorbing of EUV radiation. However, there is limited understanding about how they behave under irradiation as well as what chemical and structural properties of the resist are most beneficial. In this work, we study the molecular layer deposition (MLD) of Hf- and Al-based hybrid thin film resists, known as "hafnicone" and "alucone." These materials are grown at 100 ºC using the metal precursors tetrakis(dimethylamido)hafnium(IV) and trimethylaluminum together with ethylene glycol as the organic counterreactant. Both alucone and hafnicone are tested against electron beam exposure to inform their behavior under EUV, and results show that they behave as negative tone resists. Hafnicone exhibits a sensitivity of 400 $\mu C/cm^2$ and the ability to resolve 50 nm line widths. Alucone's line patterns are more sharply defined than those of hafnicone, suggesting higher resolution. However, whereas alucone's sensitivity is 4800 $\mu C/cm^2$ using 0.125 M HCl as the developer, hafnicone's sensitivity is 400 $\mu C/cm^2$ using 3 M HCl. The MLD resists are additionally characterized via X-ray photoelectron and infrared spectroscopy to investigate the patterning mechanism, which is described in the context of classical nucleation theory. This study of hafnicone and alucone hybrid MLD offers new insight into structural features of an MLD film that can lead to desired EUV-responsive behavior. This insight may accelerate the development of vapor-deposited inorganic resists for use in electron-beam and EUV lithography.

11:45am **EM-WeM-16 High-resolution EUV Lithographic Patterning Characteristics of InO_x-PMMA Hybrid Photoresist Generated by Vapor-phase Infiltration***, A. Subramanian,* Stony Brook University*; N. Tiwale,* Brookhaven National Laboratory*; W. Lee,* Stony Brook University*; K. Kisslinger, M. Lu, A. Stein,* Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas*; **Chang-Yong Nam**,* Brookhaven National Laboratory/Stony Brook University

Continuing extreme downscaling of semiconductor devices is essential for high performance and energy efficiency of the current and future microelectronics. Adoption of extreme ultraviolet lithography (EUVL) is poised to drive the device miniaturization into the angstrom era in near future. However, there are several material-related challenges in EUVL, and one of them is the need for developing improved EUV photoresists that can feature simultaneously high sensitivity, resolution, and etch selectivity. One strategy being explored in the field is to synthesize inorganic-containing hybrid resists that utilize high EUV sensitivity and etch resistance of inorganic elements. However, currently available hybrid EUV photoresists are mostly chemically synthesized, requiring complex and slow development and processing steps for production or modification of resist properties, while suffering from a short shelf-life. Additionally, most of the reported systems are negative-tone, crosslinking resists, which are capable of patterning line gratings or pillars but require multiple exposures or complex processing for contact-hole patterning in memory devices. In this work, we demonstrate a new, positive-tone, organic-inorganic hybrid EUV resist that delivers the high-resolution EUVL and electron-beam lithography (EBL) patterning capability combined with high etch resistance and Si etch selectivity. The new resist, poly(methyl methacrylate) infiltrated with indium oxide (PMMA-InO_x), is generated via vapor-phase infiltration (VPI)–a gaseous material hybridization technique derived from atomic layer deposition (ALD). The weak binding nature of the gaseous indium precursor, trimethylindium (TMIn), to the carbonyl group in PMMA allows the synthesis of hybrids with inorganic content distributed uniformly across the thickness of the resist. The new hybrid resist achieves: (a) high EUVL and EBL sensitivities as low as 18 mJ/cm^2 and 300 $\mu C/cm^2$, respectively, (b) high-resolution positive-tone EUVL patterning capability (e.g., 40 nm half-pitch line-space and 50 nm diameter contact hole patterns), and (c) high Si etch selectivity (>30 – 40), when combined with optimized pre- and post-patterning resist process strategies comprising underlayer application and post-development descum procedures for addressing InO_x residues. The results not only hint at the potential of VPI-based ex-situ hybridization in developing novel hybrid EUV photoresists but also can pave the way for using infiltration-synthesized hybrid thin films as reliable positive-tone EUVL photoresists without chemical amplification.

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