Thin Films
Room 317 - Session TF2-WeM

VSHOP Applications II, Semiconductor Manufacturing

Moderators: Dr. Jeffrey Elam, Argonne National Laboratory, **Dr. April Jewell**, Jet Propulsion Laboratory

11:00am **TF2-WeM-13 Molecular Layer Deposition of Polyurea Film and their Role in Sidewall Passivation during Reactive Ion Etching in HF Plasmas**, ***Sumit Agarwal***, Colorado School of Mines **INVITED**

Over the last few years, HF-containing plasmas have been widely used for etching of Si-based dielectrics for various applications, including in the fabrication of 3-D NAND memory devices. During SiN_x etching with HF plasma, ammonium fluorosilicate (AFS) forms as a transient byproduct significantly influencing the etch behavior. While AFS formation during SiN_x etching has been known for several decades, the underlying mechanism for its formation and removal remains unclear. In this study, we have used *in situ* attenuated total reflection Fourier-transform infrared spectroscopy to study the changes in the chemical boning on the SiN_x surface during reactive ion etching, along with the AFS formation and removal dynamics. We will show that a thin polyurea layer grown conformally by molecular layer deposition can be used to protect the sidewalls during etching of SiO_2/SiN_x stacks in high-aspect-ratio structures. We will demonstrate the impact of the MLD film on etching of the underlying SiN_x and SiO_2 films in a direct versus remote HF plasma, and HF gas. We will also show how the polyurea film degrades in a plasma environment and how it influences the formation of AFS.

11:30am **TF2-WeM-15 Realizing Controlled Porosity in Atomic Layer Deposited Metal Oxides**, ***Nicholas Strandwitz***, Lehigh University

Atomic and molecular layer deposition (ALD, MLD) techniques boast precise control of film thickness, conformal growth, and a wide range of material compositions.Generally, ALD and MLD thin films are non-porous, yet introduction of porosity would enable a wide range of uses ranging from catalysis to low-k dielectrics for electronics.Here, we have examined the purposeful inclusion of organic molecules including bifunctional and monofunctional alcohols during the MLD/ALD process and their subsequent removal using thermal and/or UV treatment to induce porosity.We examined the evolution of various physical and electrical properties with thermal treatment as well as the composition of these films.We found that the density and dielectric constant of these materials are smaller than the parent dense ALD oxides.This strategy is thus promising for tailor made dielectrics based on sequential self-limiting surface reactions characteristic of the ALD and MLD processes.This development parallels other methods for forming porous inorganic oxides such as terpinene inclusion in silicon-based dielectrics or block copolymer templating of inorganic solids.

11:45am **TF2-WeM-16 Coordination-Driven Ambient Infiltration of Silicon and Germanium Precursors for the Synthesis of Polymer–Inorganic Hybrid Materials**, ***Shaghayegh (Poppy) Abtahi***, Iowa State University

Block copolymer (BCP) self-assembly offers a scalable route to nanoscale pattern generation; however, pattern transfer remains one of the most significant challenges limiting its adoption in semiconductor manufacturing. While self-assembled polymer morphologies can be readily formed, translating these patterns into functional materials typically requires additional steps such as selective polymer removal and metal deposition to generate etch-resistant inorganic features. These approaches often involve elevated temperatures, highly reactive precursors, or multi-step processing, which constrain materials compatibility and process flexibility. Here, we demonstrate a coordination-driven vapor infiltration approach that directly forms inorganic hard masks at room temperature and atmospheric pressure. Poly(4-vinylpyridine) (P4VP) selectively reacts with volatile Group-14 precursors, including chlorosilanes and chlorogermanes, through N→Si coordination, producing polymer–inorganic hybrids without thermal activation or vacuum cycling. Solid-state 29Si NMR, FTIR, and Raman spectroscopy confirm the formation of hypercoordinate silicon species confined within the polymer matrix. This chemistry is applied to PS-b-P4VP block copolymer thin films, where infiltration occurs exclusively within the P4VP microdomains. Selective reinforcement of these domains enables the formation of metalloid-based inorganic hard masks that preserve the native morphology after removal of the organic template. Because the inorganic mask is generated during infiltration, the process simplifies pattern transfer and avoids the thermal budgets and precursor limitations associated with conventional ALD-based infiltration methods.

12:00pm **TF2-WeM-17 Negative-Tone PMMA-InOx Hybrid Resist Prepared by Sequential Infiltration Synthesis**, ***Jiwoong Ham***, *Minkyung Ko, Young Heon Kim,* Chungnam national university, Republic of Korea*; Hyeong-U Kim,* Korea Institute of Machinery and Materials, Republic of Korea*; Nari Jeon,* Chungnam national university, Republic of Korea

As the semiconductor industry demands ever-smaller critical dimensions, extreme ultraviolet (EUV) lithography has become essential for next-generation patterning. However, conventional organic resists suffer from poor sensitivity under EUV exposure; therefore, hybrid resists have emerged as a promising strategy to address this challenge. In this work, we prepared a hybrid resist via sequential infiltration synthesis (SIS) into poly(methyl methacrylate) (PMMA) using trimethyl indium and trimethyl gallium as metal precursor, with water and ethylene glycol as co-reactants. Due to the scarcity of EUV light sources, electron beam lithography (EBL) was employed as a surrogate tool to evaluate resist performance. Compared to pristine PMMA, SIS resists exhibit improved sensitivity for negative tone behavior and achieve high-resolution patterning down to sub-50 nm linewidth. To investigate the mechanism of improved sensitivity, μ-Raman spectroscopy, μ-X-ray photoelectron spectroscopy, scanning transmission electron microscopy, and electron energy loss spectroscopy were employed. Based on the comprehensive characterization data, we propose molecular-level structural model of the PMMA–InO_x hybrid resist that explains its enhanced sensitivity.

Author Index

Bold page numbers indicate presenter