Emerging Materials
Room Tamna Hall BC - Session EM-TuM

Molecular Layer Deposition & Hybrid Materials I

Moderators: Jin-Seong Park, Hanyang University, **Henrik Pedersen**, Linköping University, Sweden

10:45am **EM-TuM-12 Zeolite-Like Frameworks Created by ALD/MLD as an All-Dry Resist Technology**, ***Howard Fairbrother,*** Department of Chemistry, Johns Hopkins University*; Peter Corkery, Kayley Waltz,* Department of Chemical and Biomolecular Engineering, Johns Hopkins University*; Patrick Eckhert,* Department of Chemistry, Johns Hopkins University*; Michael Tsapatsis,* Department of Chemical and Biomolecular Engineering, Johns Hopkins University **INVITED**

The drive to further decrease microelectronic device dimensions has led to the expansion of extreme ultraviolet lithography (EUVL) and EBL processes which require next generation resist materials to maximize feature resolution and improve product throughput. Conventional solvent-based resist processes use organic resists which typically requiring time consuming baking steps and generate of organic solvent waste. Furthermore, mechanical stress induced by solution-based development can lead to pattern collapse, limiting the maximum possible density of patterned features. The process described herein avoids the use of, and some issues associated with, organic solvents by depositing films using ALD/MLD to produce amorphous films from 2-methylimidazole and diethylzinc that are chemically similar to zeolitic imidazolate framework-8 with sub-nanometer roughness. Following electron irradiation, areas of the film which were exposed to the electrons maintain the C:N:Zn ratio of the original film and are rendered resistant to etching by vapor phase 1,1,1,5,5,5-hexafluoroacetylacetone (hfacH). In contrast, unexposed areas can be readily removed by exposure to hfacH vapor at 120 °C, demonstrating the efficacy of aZnMIm films as a negative tone resist. The low temperature thermal etching conditions are notable, as the typical requirement of high temperatures in other dry etching processes can be difficult to implement in nanofabrication processes. The use of a molecular etchant (hfacH) also avoids limitations of plasma-based processes. aZnMIm films deposited by atomic/molecular layer deposition (ALD/MLD), patterned with electron beam lithography (EBL), and developed with hfacH achieved well-resolved 22 nm thick, 30 nm pitch lines. Sensitivity, contrast, and critical dimensions of the patterns created on silicon substrates and patterned at 30 keV are determined to be 37 mC cm−2, 0.87, and 29 nm, respectively. This work introduces a new direction for solvent-free resist processing, offering the prospect of scalable, high-resolution patterning techniques. Future work will explore substitution of the zinc metal centers for more EUV absorptive metals and the introduction of more reactive groups onto the organic linkers to increase resist sensitivity.

11:15am **EM-TuM-14 Atomic Layer Regulation of MIL-53 Metal-Organic Framework as Interconnect Low-k Dielectrics**, ***Fan Yang,*** *Jisheng Song, Rong Chen,* Huazhong University of Science and Technology, China

Metal-organic frameworks stand out as one of the promising low-k dielectrics candidate to alleviate the delay caused by interconnect resistance of metal wire and capacitance of interlayer dielectrics (RC delay) in the context of the ever-denser and miniaturized integrated circuits. However, achieving nanoscale control over thickness of the fabrication of MOF thin-films is a critical requirement for subsequent lithography and metallization steps as well as of adequate mechanical strength. Therefore, precision preparation and modification of MOF-based dielectric film becomes an urgent need.

In this work, we report a synthetic strategy of ultra-low k (1.93 at 1 MHz) MIL-53 dielectrics by converting atomic layer deposited Al_2O_3 seed layer via microwave-assisted solvothermal method, where nanometer-scale regulated MIL-53 film can be obtained due to the linear dependence of the thickness of MIL-53 film on the Al_2O_3 seed layer. The synthesized the MIL-53 film also exhibits excellent hydrophobic properties and stability, with the dielectric constant remaining stable even after 12 days of aging, reflecting its potential as a dielectric insulating material. In addition, additional Al-O bond enhanced structures were formed in the MIL-53 framework by gas phase atomic layer infiltration (ALI) modification. After ALI treatment, the Young's modulus of MIL 53 increased by 27.7% (from 19.5 GPa to 24.9 GPa), hardness increased by 64.7% (from 0.17 GPa to 0.28 GPa), while only slightly increased on dielectric constant (from 1.93 to 2.32). The MOF film fabrication ALI modification strategy holds great promise for MOF based film synthesis and modification for interconnect dielectrics and various applications.

References

1. Atomic Regulation of Metal–Organic Framework Thin Film for Low-k Dielectric. Meng Cao, Jisheng Song, Haonan Ren, Fan Yang, Rong Chen,*Chem. Mater. 2024, 36, 22, 11160–11169*.

11:30am **EM-TuM-15 Nanolaminated Films with Negative Capacitance Fabriacted by ALD**, ***Xiang Yang Kong,*** School of Materials Science Engineering Shanghai Jiao Tong University, Shanghai 200240, China

The relization of negative capacitance (NC) behavior has long attracted the interests of electrical engineers. Some evidences have been demonstrated by examining the NC response resulting from adding a ferroelectric layer in series with a dielectric. In this talk, we fabricate a series of multilayered films with negative capacitance by ALD. The NC behavior occurs at the hetero-interfaces between the ferroelectric and paraelectric nanolayers.Regarding NC in hafnia-based materials, the oxygen-deficiency is accounted for unstable features as well as their ferroelectric and dielectric properties. We proposed the mobile ions at interfaces could enhance the stability of NC effects with the induced polarization.Moreover, we also lay out the way for scaling the NC FET nanoelectronics down to 2.5–5nm ferroelectric gate as well as giant density of energy storage.

11:45am **EM-TuM-16 Thermal Annealing of Molecular Layer-Deposited Tincone : Unveiling Sulfur's Structural Impacts in Graphitic Carbon Formation**, ***Gi-Beom Park,*** *Hyolim Jung, Hae Lin Yang, Ji-Min Kim,* Hanyang University, Korea*; Chang-Kyun Park,* Hanyang University, Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea, Republic of Korea

As the scaling down of semiconductors based on Moore's Law continues, efforts to introduce 2D graphitic carbon is being considered for use as a Cu diffusion layer and as top/bottom capping electrodes for Storage Class Memory (SCM), leveraging its high electrical conductivity and small geometric pore size to prevent diffusion between layers.[1,2] Additionally, it has the advantage of low chemical reactivity, making it suitable as an inhibitor in Area-Selective Deposition (ASD).[3] Both Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have been studied as methods for depositing graphitic carbon. However, the direct deposition of graphitic carbon on dielectric layers using CVD is limited, requiring a transfer process after deposition on substrates like Cu or Ni.[4] On the other hand, using ALD to deposit on dielectrics increases the sp^3 bonds, which compromises the benefits of sp^2 bond-based carbon.[5] Therefore, research is needed on deposition methods that can directly deposit graphitic carbon on dielectrics, regardless of the substrate. Using Molecular Layer Deposition (MLD) to deposit metalcone thin films followed by thermal annealing has confirmed the formation of graphitic carbon as metal atoms are eliminated.[3] Additionally, metalcone thin films can be effectively deposited on dielectric layers, providing the advantage of forming graphitic carbon regardless of the substrate. However, research on the formation of graphitic carbon through the thermal annealing of metalcone thin films has been limited to organic precursors with hydroxyl groups, such as hydroquinone (HQ). Therefore, it is necessary to study the graphitization behaviors influenced by the composition variations depending on different organic precursors.

In this study, tetrakis(dimethylamido)tin (TDMASn) and 4-mercaptophenol (4MP) were used to deposit tincone, followed by thermal treatment to explore the effect of sulfur within the metalcone thin film on the formation of graphitic carbon after thermal annealing. The MLD tincone films were deposited at 100 °C without impurities, then vacuum post-annealed in a tube furnace to induce graphitization. Spectriscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy were employed to investigate the effect of thermal annealing on the tincone thin film. As a results, atomic concentration of Sn decreased as increasing annealing temperature but Sulfur deteriorate graphite structure above annealing temperature of 500℃. Threrefore, it is important to find appropriate annealing condition by composition of metalcone thin film.

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