Area Selective ALD
Room Hall 3E - Session AS-TuM
Selective ALD

Moderators: Han-Bo-Ram Lee, Incheon National University, **Angel Yanguas-Gil**, Argonne National Lab

10:45am **AS-TuM-12 A Novel SMI for AS-ALD***, **Molly Alderman**, A. Upadhyay,* Carleton University, Canada*; M. Griffiths, K. Blakeney, D. Agnew, P. Lemaire, J. Smith, D. Hausmann,* LAM Research*; S. Barry,* Carleton University, Canada*; D. Mandia,* LAM Research

Area selective atomic layer deposition (AS-ALD) presents a means to achieve the ever-increasing architectural density and decrementing feature sizes demanded by Moore's law beyond what is possible when patterning by photolithography alone. With inherently selective ALD processes being rare, the use of surfactants to promote or inhibit growth of films has gained traction.[1] In particular, small molecule inhibitors (SMIs) are preferable to self-assembled monolayers (SAMs) for modification of growth behaviour owing to their smaller size, improved thermal characteristics, vapour phase adsorption, and (when compared to the most common SAMs) lack of heavy heteroatoms, in particular sulfur, preventing film contamination.[2]

We have synthesized a family of novel polyfluorinated isonitriles with different chain lengths for use as a SMI in AS-ALD. As an example, Long Chain Inhibitor is readily synthesized in two steps from the amine and is volatile, with a 1 Torr vapour pressure at 33 °C. This compund shows promising selectivity for adsorption to metals over oxides as measured via quartz crystal microbalance (QCM), saturating gold with a surface density of 62 ng/cm^2 (0.81 $molecules/nm^2$) with concurrently negligible adsorption on alumina (Figure 1). The synthesis and thermal characterization of several fluorinated isonitriles will be discussed. Their selectivity for metal surfaces by QCM, as well as ToF-SIMS mapping on metal/SiO_2 patterned substrates will be shown to demonstrate selectivity, with excellent resolution provided by the high fluorine content of the molecule. Selective inhibition of zinc oxide ALD will also be discussed and selectivity values will be reported.

References

(1) Parsons, G. N.; Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.***2020**, *32* (12), 4920–4953. https://doi.org/10.1021/acs.chemmater.0c00722.

(2) Yasmeen, S.; Ryu, S. W.; Lee, S.-H.; Lee, H.-B.-R. Atomic Layer Deposition Beyond Thin Film Deposition Technology. *Advanced Materials Technologies***2023**, *8* (20), 2200876. https://doi.org/10.1002/admt.202200876.

11:00am **AS-TuM-13 Atomic Layer Plasma Treatment for Area-Selective Atomic Layer Deposition of High-Quality SiO_2 Thin Film***, **Sanghun Lee**, S. Seo, T. Kim, H. Yoon, S. Park, S. Na, J. Seo,* Yonsei University, Republic of Korea*; W. Noh,* Air Liquide, Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) has been intensively studied due to its demonstrated versatility in recent nanotechnology applications. The priority focus in AS-ALD is achieving the desired selectivity; thus, most studies to date have concentrated on the reaction mechanism of ALD on the growth/non-growth substrate or sought novel methodologies to resolve challenges in its implementation in high-volume manufacturing. On the other hand, the qualities of film deposited by AS-ALD were usually not highlighted. In this work, we studied the AS-ALD approaches that could enhance the selectivity and film quality simultaneously. We developed AS-ALD SiO_2 on SiO_2 whereas SiO_2 was not grown on SiN_x. NH_3 plasma pre-treatment was employed to functionalize SiN_x surface with more –NH species which are known for their lower reactivity toward Si precursors. The results show that NH_3 plasma pre-treatment is effective in increasing selectivity, but the plasma condition needs to be controlled to avoid inducing damage to the SiN_x surface, which could offer reactive sites for precursor adsorption. We carried out ALD supercycle of NH_3 plasma pre-treatment and ALD SiO_2 to achieve higher selectivity. When the number of NH_3 pre-plasma treatment cycles was increased, the growth of SiO_2 on SiN_x was further delayed. Furthermore, layer-by-layer NH_3 plasma pre-treatment densified the SiO_2 film owing to ion bombardment, as revealed in etching characteristics and x-ray reflection spectra. Moreover, NH_3 plasma pre-treatment did not result in incorporation of nitrogen into growing SiO_2 film as analyzed by x-ray photoelectron spectroscopy. Consequently, atomic layer NH_3 plasma pre-treatment enabled a higher selectivity and improved SiO_2 film quality, as evaluated by the electrical property measurement of metal-oxide-semiconductor capacitor.

11:15am **AS-TuM-14 Enhancing Selectivity for AS-ALD of MoO_2 through Hydrogen Treatment: Strategy of Surface Cleaning and Expanding Deactivated Areas***, **Hae Lin Yang**, J. Kwon, C. Park,* Hanyang University, Korea*; S. Lee, B. Kim, C. Jung, H. Lim,* Samsung Electronics Co., Inc., Republic of Korea*; J. Park,* Hanyang University, Korea

Recently, in the field of DRAM capacitors, the demands for precisely depositing MoO_2 thin films for resolving the high leakage issue between high-k dielectric and TiN electrodes, onto TiN without additional patterning[1]. To meet these demands, Area selective atomic layer deposition (AS-ALD), which allows selective deposition on certain areas without undesired deposition on adjacent areas, is essential. Also accomplish the high selectivity of high-resolution films with high spatial resolution, the introduction of inhibitors is needed especially small molecular inhibitors (SMIs). SMIs consist of inert tail portions composed of single molecules, enabling them to have small sizes suitable for narrow lines at the nanometer scale. However, SMIs typically have short tail groups that cannot undergo van der Waals interactions, and they cannot densely cover the substrate surface due to steric hindrance from adjacent adsorbed SMIs during precursor adsorption[2]. Therefore, considerations regarding the treatment of unadsorbed areas and the removal of remaining reactive groups after SMI adsorption are necessary. To address this, we added a hydrogen treatment process during the AS-ALD process of MoO_2 using TCPS [$C_6H_5SiCl_3$] and DMA-TMS [$(CH_3)_3SiN(CH_3)_2$] as SMIs and analyzed the effects of hydrogen treatment on surface properties and selectivity using XPS, WCA, and AES mapping. Additionally, we calculated reaction energies for each adsorption step and final forms for each SMI-adhered surface using DFT and RSA simulations. TCPS, owing to its aromatic phenyl ring, covers a wider range of SiO_2 surfaces than DMA-TMS. However, only two out of three Cl ligands react, leaving about 1.4% of the remaining Cl ligands after TCPS adsorption, increasing the surface energy and acting as adsorption sites for Mo precursors. However, by adding a hydrogen treatment cycle during the process, all remaining Cl ligands were removed, resulting in a 13° increase in WCA and a dramatic increase in selectivity from 61% to 96%. Furthermore, hydrogen treatment not only removed residual impurities but also reduced exposed -OH groups on the surface by converting them to -H, as confirmed by the results of hydrogen treatment added during the DMA-TMS process. Despite the absence of impurities to be removed, the WCA increased by approximately 7° after hydrogen treatment, and the selectivity also increased from 84% to 94.5%. In this way, appropriate treatments during AS-ALD processes, though simple, can effectively increase selectivity, enabling precise selective deposition in desired areas even in complex structures.

11:30am **AS-TuM-15 Contra-Selective Deposition of SiO_2 on Metals***, **Chad Brick**, T. Ogata,* Gelest, Inc

In recent years, an increasing number of area selective processes have been developed for the deposition of dielectric films on dielectric layers. However, reports of the selective deposition of dielectric films on metal regions of a substrate are comparatively rare, typically involving the deposition of high-k dielectric films with significantly different chemistry with respect to the target low-k non-growth areas such as SiO_2 or SiN. In this study, a series of heteroatom-containing silanes with inherent selectivity towards metals over SiO2 and SiN and their conversion to SiO2 via plasma-enhanced atomic layer deposition have been investigated. It will be shown that under appropriate conditions, indefinitely thick films of SiO2 can be selectively grown on metals such as copper and cobalt with pre-existing native or thermal silicon dioxide as the non-growth substrate. Mechanisms of this unusual "contra-selectivity", with a film growing not only on a material other than itself with its unblocked self as a non-growth surface, but also continuing to grow to arbitrary thickness despite the near-identical nature of the growth and non-growth surfaces after the first few deposition cycles, will be discussed.

11:45am **AS-TuM-16 Photoluminescent Graphene-Lanthanide Heterostructures via Direct Laser Writing and Area-Selective Atomic-Molecular Layer Deposition***, **Aleksei Emelianov**, K. Mentel,* University of Jyväskylä, Finland*; A. Ghazy,* Aalto University, Finland*; A. Johansson,* University of Jyväskylä, Finland*; M. Karppinen,* Aalto University, Finland*; M. Pettersson,* University of Jyväskylä, Finland

Area-selective atomic-molecular layer deposition (AS-ALD/MLD) is a promising "bottom-up" alternative to the current nanopatterning techniques [1,2]. It has been used on a variety of materials, including the growth of two-dimensional materials (2DM). While there are examples of AS-ALD being used on 2DM, the approach of combining it with AS-MLD is still mostly unexplored. Due to the inherent 2D nature, the surface of 2DM does not provide sufficient reactive sites for the chemisorption of ALD/MLD precursors compared with traditional microelectronics. Functionalization of certain surface areas is required to provide the selective growth of materials. Recently, we have overcome the chemical inertness of graphene to ALD precursors by local activation using direct femtosecond laser two-photon oxidation (TPO) [3] for selective ZnO deposition [4].

In this study, we guided the growth of Eu-organic thin films on top of single-layer graphene via TPO. We achieved high homogeneity and more than 90% selectivity in locally activated predefined regions for Eu films up to 15 nm. The polymer used for graphene transfer significantly affects the selectivity of the ALD/MLD process, as it might leave residues and promote unnecessary deposition in pristine graphene areas. The fabricated graphene/Eu-organic thin films exhibited high photoluminescence at 615 nm even when excited with a 532 nm laser. The films are suitable for various applications in optoelectronics, sensors, and LEDs.

References:

[1] G. N. Parsons, R. D. Clark, Chemistry of Materials, 32, 4920 (2020).

[2] J. Multia, M. Karppinen, Advanced Materials Interfaces, 9, 2200210 (2022).

[3] J. Aumanen, A. Johansson, J. Koivistoinen, P. Myllyperkiö, M. Pettersson, Nanoscale, 7, 2851 (2015).

[4] K. K. Mentel, A. V. Emelianov, A. Philip, A. Johansson, M. Karppinen, M. Pettersson, Advanced Materials Interfaces, 9, 2201110 (2022).

Author Index

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