Area Selective ALD
Room Regency Ballroom A-C - Session AS2-TuM
Inhibitors and ASD

Moderator: Prof. Dr. Stacey Bent, Stanford University

10:45am **AS2-TuM-12 Consequences of Random Sequential Adsorption of Inhibitor Molecules for Loss of Selectivity During ALD***, **Joost Maas**,* Eindhoven University of Technology, Netherlands*; I. Tezsevin,* Eindhoven University of Technology, Turkey*; M. Merkx, E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

For achieving area-selective atomic layer deposition (ALD), vapor-phase dosing of small molecule inhibitors (SMIs) is currently being explored, motivated by its compatibility with industrial processing. During vapor-phase dosing, SMIs typically arrive one-by-one at random sites, leaving relatively large gaps in between the inhibitor molecules where a precursor can potentially interact with the surface. This so-called random sequential adsorption (RSA) mechanism results in partial packing (i.e., deviating from close packing) of inhibitor molecules on the non-growth area, serving as the main challenge for the development of highly-selective processes using SMIs. In this work, RSA simulations are performed to emulate the vapor-phase dosing of various di-ketone (e.g. Hacac, Hthd) and aromatic (e.g. benzene, aniline) inhibitor molecules during an ALD process.[1] The understanding of the coverage and the inhibitor packing obtained by RSA simulations gives insights into the selectivity loss during area-selective ALD processes.

To carry out the RSA simulations, density functional theory (DFT) simulations are used to determine the 2D footprint of favorable binding configurations. A surface functionalized with inhibitor molecules is simulated by placing molecules one-by-one at random sites until the surface is saturated. Simulations were performed for different di-ketones to investigate the influence of the inhibitor size on the packing. It was found that the size of the inhibitor plays a critical role in achieving a high packing density, with the bulky 2,2,6,6,-Tetramethyl-3,5-heptanedione (Hthd) inhibitor giving a lower packing density but a higher covered area as compared to acetylacetone (Hacac). Furthermore, the surface structure of the non-growth area influences the density of inhibitor molecules. For example, benzene packs with a relatively high density on Ru because it matches the lattice constant. The distribution of the available sites for ALD precursor adsorption are estimated as a measure for precursor blocking, allowing for a comparison to experimental ellipsometry and infrared spectroscopy data on area-selective ALD of SiO_2 and TiN.[2, 3] Based on this analysis, insight is also obtained into the influence of the precursor choice on the selectivity loss, illustrating that area-selective ALD with high selectivity requires a complementary set of inhibitor and precursor molecules.

[1] Li *et al., J. Vac. Sci. Technol. A***40**, 062409 (2022)

[2] Merkx *et al.*, *J. Phys. Chem. C*, **126**, 4845 (2022)

[3] Merkx *et al.*, *Chem. Mater.*, **32**, 7788 (2020)

11:00am **AS2-TuM-13 In-Situ Formation of Inhibitor Species Through Catalytic Surface Reactions During Area-Selective Tan ALD***, **Marc Merkx**, T. Janssen, I. Tezsevin, R. Heinemans, R. Lengers,* Eindhoven University of Technology, Netherlands*; J. Chen, C. Jezewski, S. Clendenning,* Intel*; E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Recently, small molecule inhibitors (SMIs) have been gaining attention, as an alternative to self-assembled monolayers (SAMs), for achieving area-selective atomic layer deposition (ALD) due to their compatibility with vapor-phase processes and plasma-assisted ALD. However, in contrast to SAMs, vapor-phase application of SMIs typically results in a disordered inhibitor layer, and therefore a lower inhibitor coverage.[1] This lower coverage makes it more challenging to achieve a high selectivity. In previous work, aniline was found to be an excellent inhibitor molecule for enabling area-selective ALD of TiN and TaN with metal/dielectric selectivity.[2] In this contribution, the precursor blocking mechanisms by aniline inhibitor molecules are studied using in-situ reflection adsorption IR spectroscopy (RAIRS) to understand what makes aniline an effective inhibitor.

The RAIRS spectra show that aniline undergoes catalytic surface reactions for substrate temperatures above 250 °C. These reactions turn the adsorbed aniline into C_6H_x adsorbate species, while NH_3 and potentially H_2 desorb from the surface. For the same temperatures (>250°C), a much higher selectivity was observed for area-selective TaN ALD using aniline as inhibitor, with respect to lower substrate temperatures. These observations suggest that the catalytic surface reactions play an important role in improving precursor blocking by the aniline inhibitor layer. The improvement in the selectivity is likely caused by the formation of a more carbon-rich inhibitor layer. Such carbon-rich layers have been shown to be effective at blocking ALD precursor adsorption.[3,4] More importantly, the catalytic surface reactions chemically alter the dosed inhibitor on the surface, i.e. new inhibitor species are formed in-situ during area-selective ALD. These reactions therefore provide a new strategy for forming inhibitor layers, enabling the use of inhibitor species that are otherwise more challenging or impossible to dose in vapor-phase.

[1] Li et al., J. Vac. Sci. Tech. A 40, 062409 (2022)

[2] Merkx et al., Chem. Matter. 32, 7788 (2020).

[3] Stevens et al., Chem. Matter. 30, 3223 (2018)

[4] Vervuurt et al., Adv. Mater. Interfaces 4, 1700232 (2017)

11:15am **AS2-TuM-14 Area Selective Atomic Layer Deposition of Ru and W Using W Precursor Inhibitor***, **Mingyu Lee**, T. Nguyen Chi, L. Trinh Ngoc, B. Gu, H. Lee,* Incheon National University, Republic of Korea

Area Selective Atomic Layer Deposition (AS-ALD) is a method which can inhibit or promote the following growth by changing surface property. AS-ALD has been considered as an approach to overcome the current challenges in nanofabrication for 3D Si devices which can't be achieved by the conventional photolithography and etching processes. For AS-ALD, self-assembled monolayers (SAMs) have been widely used to control surface property for inhibition and promotion. However, the thermally unstable organic ligand and the size of SAMs are the main obstacles to commercialize AS-ALD using SAMs. Precursor inhibitor (PI) can be an alternative material to SAMs for this purpose since the size of precursors are usually smaller than those of SAMs and the precursors are already used for the commercialized fabrication process. In this study, $EtCpW(CO)_3H$ precursor is utilized as an inhibitor to block following Ru and W ALD on a W surface. Density functional theory (DFT) calculation results indicated that the W PI can adsorb on the W surface and has unfavorable energy to the following precursors and reactants adsorptions. Monte Carlo (MC) simulation was used to calculate the surface coverage and physical interactions between the metal precursors and the W PI. The physical steric hindrance effect played an important role of the W PI adsorptions, the MC simulation showed that surface coverage can be improved by multiple exposure of the PI divided by nitrogen purging step. These results showed high consistent with the experiments analyzed by water contact angle (WCA) and transmission electron microscopy (TEM). By combining the theoretical and experimental results, the blocking mechanism of the W PI against Ru and W could be explained. We believe that the conceptof PI for AS-ALD could be applied to overcome various challenges in the patterning process of Si device fabrication.

11:30am **AS2-TuM-15 Partial Surface Passivation for Controlled Growth and Conformality Improvement on High Aspect Ratio Features Using Small Molecule Inhibitors***, **Kok Chew Tan**, C. Yeon,* Soulbrain, Republic of Korea*; J. Kim,* Hongik University, Republic of Korea*; J. Jung, S. Lee, T. Park, Y. Park,* Soulbrain, Republic of Korea*; B. Shong,* Hongik University, Republic of Korea

The motivation to keep semiconductor industry scaling has seen devices such as DRAM and VNAND continue to move vertically. Unlike 2D features, deposition of excellent film properties using atomic layer deposition (ALD) is increasingly challenging on high aspect ratio (HAR) 3D features. Various small molecule inhibitors and new deposition strategies with a particular emphasis on achieving conformal thin films are actively being investigated.

In this work, we have identified potential small molecule inhibitors suitable for application in different types of ALD films (e.g. oxide, nitride and metal films). Surface passivation using these inhibitors could overcome the limitations of conventional ALD in 3D nanofabrication such as poor conformality, seam formation and edge placement error in top-down approach nanofabrication. These inhibitors are introduced into the deposition chamber prior to every precursor feed step to modulate surface reactivity on the top region of the trench. The blockage of top reactive sites by the inhibitors allow more diffusion-limited (precursor) deposition reaction at the bottom trench, leading to improved film conformality on HAR features. Effective in-situ removal of the adsorbed inhibitors in each

reactant feed step is another merit of this work that could prevent impurity incorporation.

Our work using these small molecule inhibitors has demonstrated lower growth per cycle, signifying growth inhibition and visible conformality improvement in nitride and oxide films, achieving conformality of more than 90% on HAR features **[1, 2]**. These experiment results were further elucidated by density functional theory (DFT) calculations with a focus on the roles of inhibitor on SiN_x surface and its reaction with reactant, NH_3**[3]**. The inhibition ability of the inhibitor was evidenced by the DFT results in term of activation energy. These DFT results also showed feasible reaction of NH_3 with the adsorbed inhibitors on the surface, consequently removing unwanted impurity contamination and regenerating the $-NH_2$ functional groups on the surface.

References:

1. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).
2. K.C. Tan, J. Jung, S. Kim, J. Kim, S.J. Lee and Y. Park, AIP Advances 11, 075008 (2021).
3. J. Kim et. al. (2022, Oct 26-28). Mechanism for Partial Passivation of Silicon Nitride Surface with t-Butyl Chloride. Fall Conference of the Korean Institute of Metals and Materials, Jeju Island, Republic of Korea

11:45am **AS2-TuM-16 Fundamental Surface Chemistry Considerations for Selecting Small Molecule Inhibitors for AS-ALD***, A. Mameli,* TNO Science and Industry, the Netherlands*; **Andrew Teplyakov,*** University of Delaware

Current atomically-precise processing methods, specifically area-selective atomic layer deposition (AS-ALD), are firmly dependent on the difference in reactivity between growth and non-growth surfaces. However, this selectivity is always lost after certain number of ALD cycles, and etch-back and/or passivation of the surface reactive sites or defect sites with small molecule inhibitors (SMI) is required.

This talk will focus on a connection between surface chemistry of potential SMI on target (mostly oxide) materials and the selection criteria for using these organic molecules in realistic processes on realistic surfaces. Many of the concepts of the classical surface chemistry that had been developed over several decades can now be applied to design such SMIs. We will consider the roles of selectivity, chemical stability of a molecule on a specific surface; volatility, fast attachment reaction kinetics, steric hindrance, geometry and packing strength of adsorption as detailed by interdisplacement to determine the most stable SMI, minimal number of various binding modes, precursor of choice for material deposition. We then describe how to down-select appropriate SMI based on their properties. We will specifically focus on various acids, alcohols, and diketones and consider several materials, including ZnO and TiO_2.

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