Area Selective ALD
Room Event Hall - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-2 Advancements in Area-Selective Deposition by Merck: From Fundamental Principles to Industrial Applications*, **Isiah Liu,*** The Electronics business of Merck KGaA Darmstadt, Germany*; Lanxia Cheng, Tingmin Wang, Matthew MacDonald, Bhushan Zope,* Merck KGaA, Darmstadt*; Chang-won Lee,* Merck KGaA, Darmstadt, Republic of Korea*; Masashi Jinguji, Xinjian Lei,* Merck KGaA, Darmstadt

Area Selective Deposition (ASD) processes have gained significant attention due to the limitations of current lithographic techniques in fabricating advanced semiconductor devices, particularly as device dimensions continue to shrink. For the development of future semiconductor nodes, a critical process is required to selectively grow thin films on specific surfaces while preventing deposition on others. This process must effectively differentiate between surfaces to ensure precise material deposition. To address these challenges, Merck has developed systematic concepts based on the surface reactions involved in selective deposition, which require a comprehensive understanding of surface chemistry and the reactivity of inhibitors to passivate non-growth areas. The inhibitor layer plays a crucial role in the ASD process by acting as a protective barrier, selectively preventing deposition on undesired regions of the substrate while ensuring material growth occurs only on the targeted surfaces. These surface reactions were initially explored through molecular modeling and subsequently confirmed through application tests and in-situ metrologies. Through extensive studies, the optimal selection of inhibitors, coupled with the development of the ASD process, has been successfully achieved, enabling precise control over material deposition in advanced semiconductor fabrication. This progress has led to the development of several novel ASD processes that have attracted significant interest within the industry, demonstrating the ability to selectively passivate dielectric (SiO2, Si3N4, Si) and metal (Cu) substrates. This breakthrough offers a promising solution for the precise control of material deposition, representing a critical advancement for the fabrication of next-generation semiconductor devices.

AS-TuP-3 Comparative Study of Experimental and DFT Calculations of Trimethylaluminium Adsorption on SiO_2, SiN, and Si for Area-Selective Deposition*, **Genki Hayashi**, Ni Zeyuan, Yumiko Kawano, Shinichi Ike, Shuji Azumo,* Tokyo Electron Technology Solutions Limited, Japan

Area-Selective Deposition (ASD) is an attractive process for semiconductor manufacturing[1]. It utilizes the differences of the surface chemical reaction between a precursor molecule and different substrates. Surface reaction simulations are useful tools for screening appropriate ASD precursors[2]. In this study, we investigated the validity of adsorption energy calculation using density functional theory (DFT) by comparing the calculation with the process outcomes.

We calculated the adsorption energy of Trimethylaluminium (TMA) molecule on H-terminated Si, OH-terminated SiO_2, and NH-, OH- and F-terminated SiN substrates (Fig1(a)). Here, TMA is a well-known precursor that is often used for Al_2O_3 deposition, and the choices of these surface terminations were based on the usual dilute HF (DHF) treatment prior to precursor introduction to remove native oxides[3]. It is widely known that H (OH) terminated surface was formed for Si (SiO_2) surface after DHF. For SiN surface, it was found from X-ray photoelectron spectroscopy (XPS) measurement (Fig1(b)) that fluorine was clearly detected on the surface, suggesting that not only OH and NH but also non-negligible amount of F was terminated on the surface, which is consistent with the previous study [3]. The calculated adsorption energy (Fig1(a)) was lower in order of the SiO_2(-OH), SiN(-OH), SiN(-NH), Si(-H), and SiN(-F) cases. This suggested that TMA is most likely to adsorb on the SiO_2(-OH) surface, whereas most unlikely to adsorb on SiN(-F) surface.

To compare the simulation results with experiments, we actually introduced TMA to Si, SiO_2, and SiN substrates in a chamber after DHF. Fig1(c) shows the XPS results (Al 2p) of these substrates after TMA flow. The largest amount of Al (resulting from TMA adsorption) was observed on the SiO_2 substrate, which agrees with the speculation from the simulation results. For SiN substrate, we also performed H_2O dipping treatment for 12.5 h at maximum after DHF, and consecutively, TMA flow experiment. As shown in Fig2(a) (XPS results), amount of fluorine decreased for 12.5-h H_2O dipping, suggesting that -F is replaced by -OH. Corresponding to this, it was found from XPS measurement (Fig2(b)) that amount of Al increased. This experimental result is consistent with the adsorption energy calculation (Fig1(a)) where TMA is more likely to adsorb on SiN(-OH) than on SiN(-F). These results demonstrate the usefulness of the DFT calculations to estimate selectivity in developing ASD.

[1]G. N. Parsons and R. D. Clark, *Chem. Mater.* 2020, 32, 4920−4953.

[2]P. P. Wellmann et al., *Chem. Mater.* 2024, 36, 7343−7361.

[3]L-H. Liu et al., *J. Phys.: Condens. Matter* 28 (2016) 094014.

AS-TuP-4 An Automated Adsorption Simulation Workflow for Efficient High-Throughput Molecule Screening for Area-Selective Deposition*, **Zeyuan Ni**, Michitaka Aita,* Tokyo Electron Technology Solutions Ltd., Japan*; Ayuta Suzki,* TEL Technology Center, America, LLC*; Genki Hayashi, Yumiko Kawano, Shinichi Ike, Shuji Azumo,* Tokyo Electron Technology Solutions Ltd., Japan

Area-selective deposition (ASD), a “chemical patterning” method that can reduce the fabrication cost and achieve novel structures beyond lithography, is gathering increasing global interests from researchers in semiconducting industry.[1–3] One of the key items to realize ASD on two specific types of areas is the selection of reactants and/or inhibitors from over thousands of candidate molecules. Compared to experiments, the first-principles simulation is a more accessible approach with lower cost and higher speed. Yet, a thorough simulation for an adsorption event requires searching for several most energetically favorable saddle points (i.e. transition states) in the potential energy surface, which makes it demanding in computation resources for high-throughput exploration.

In this work, we developed a simple surrogate automatic simulation workflow for evaluation of a molecule’s adsorption behavior on surfaces by using density functional theory (DFT) software VASP and automation packages fireworks and atomate[4]. First, we performed manual simulations of the adsorption behavior for N-(Trimethylsilyl)dimethylamine (TMSDMA) C5H15NSi on 7 types of surfaces by using the NEB method. It is found that the activation energy E_a is almost in proportion to the adsorption energy after molecule dissociation, which is denoted as E_{d_ads}. (Fig. 1) Such empirical relationship is similar to the well-known Bell-Evans-Polanyi principle[5], so we believe E_{d_ads} can serve as a reasonable surrogate metric for E_a.

Accordingly, an automatic E_{d_ads} simulation workflow that can break molecules into fragments and search for the most stable adsorption configuration automatically has been implemented (Fig. 2) and tested for 4 types of molecules on Ru and hydroxyl-terminated SiO2 (SiO2-OH) surface. For each molecule-substrate pair, multiple adsorption configurations have been investigated, from which the most stable one is chosen to represent the final adsorption energy of the molecule on the specific surface (Fig. 3). Within the 4 molecules we investigated, we find that the difference of alkynes’ adsorption energies on Ru and SiO2-OH is the largest, outperforming TMSDMA, carboxylic acids, and pyridine. Alkynes could be promising inhibitors blocking Ru surface compared to SiO2-OH.

References

[1] G.N. Parsons, and R.D. Clark, Chem. Mater. **32**(12), 4920–4953 (2020).

[2] S. Balasubramanyam, et al., ACS Mater. Lett. **2**(5), 511–518 (2020).

[3] C.T. Nguyen,et al., Chem. Mater. **35**(14), 5331–5340 (2023).

[4] G. Kresse, and J. Furthmüller, Phys. Rev. B **54**(16), 11169–11186 (1996).

[5] M.G. Evans, and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

AS-TuP-6 Optimization of Small Molecular Inhibitors for Area-Selective Atomic Layer Deposition by Controlling Alkyl Chain Length*, **EunChong Cho,*** Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Hae Lin Yang,* Hanyang University, Korea*; Jung-Hoon Lee,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea*; Youngkwon Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

This study addresses the limitations of conventional self-assembled monolayers (SAMs) in area-selective atomic layer deposition (AS-ALD) by investigating small molecular inhibitors (SMIs) for vapor-phase deposition. SMIs were designed based on trimethoxyphenylsilane (TMPS) with varying alkyl chain lengths (n = 1-6) interposed between the phenyl and silicon. The SMIs were characterized using nuclear magnetic resonance (NMR) spectroscopy and evaluated for passivation effectiveness through water contact angle (WCA) measurements on SiO2 substrates and AS-ALD experiments. The WCA of SMIs with shorter alkyl chains (n = 1-3) was higher than TMPS, while those of SMIs with longer chains (n = 4-6) were lower. To evaluate the selectivity of SMIs in AS-ALD experiments, we first deposited SMI on SiO2 and TiN substrates, followed by VO2 deposition. SiO2 was used as a non-growth area, while TiN served as a growth area. As a result, the shorter chain SMIs (n = 1-3) achieved over 85% selective inhibition efficiency on SiO2 relative to TiN, in contrast to TMPS showing ~67% efficiency. The optimal selective inhibition efficiency of about 90% was observed for n = 2. In contrast, longer chain SMIs (n = 4-6) exhibited diminishing selective inhibition efficiency, correlated well with WCA results. This study provides valuable insights for future SMI designs in AS-ALD applications, contributing to the advancement of nanoscale semiconductor fabrication techniques.

AS-TuP-7 Area-Selective Atomic Layer Deposition of Amino Silane-Based Small Molecule Inhibitor for Enhancement of Selectivity*, **Jae Hun Hwang**, EunChong Cho, Youngkwon Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is one of the next-generation technologies that enable bottom-up fabrication, in contrast to the traditional top-down fabrication used in semiconductor manufacturing. AS-ALD has the potential to reduce the number of lithographic patterning steps considerably. Furthermore, AS-ALD enables angstrom-level accuracy in specific regions of substrates with diverse chemical properties when fabricating thin film devices. In this study, we applied small molecular inhibitors (SMIs) in AS-ALD to address the issues of low volatility and uniformity in gas-phase processes of conventional self-assembled monolayers (SAMs). We compared two SMIs, trimethoxyphenylsilane (TMPS) and tri(dimethylamino)phenylsilane (TDMAPS), containing methoxides and dimethylamines as the head groups that can interact with the substrates.

The synthesized SMIs were characterized using nuclear magnetic resonance spectroscopy. SMIs were deposited using ALD, and water contact angle measurements were performed on four substrates (SiO2, SiN, TiN, and Cu) to evaluate the coverage and passivation effectiveness. After depositing a Ru film on the SMIs-coated substrate using the Ru precursor $[Ru(II)(\eta^5\text{-}C_7H_7O)(\eta^5\text{-}C_7H_9)]$, the film thickness was measured via X-ray fluorescence analysis. X-ray photoelectron spectroscopy was performed to conduct a precise elemental analysis of Ru. TDMAPS deposited on SiO2 and SiN substrates showed 100% selectivity for 150 cycles of Ru deposition, while deposition occurred on Cu and TiN substrates after a slight nucleation delay, confirming the substrate-specific chemo-selectivity. In particular, the TDMAPS-coated SiO2 and SiN showed higher selectivity of Ru precursors compared to those of TMPS, which is attributed to the of higher reaction rates amino groups with the substrate. This study demonstrates the importance of the head groups of SMIs to enhance the selectivity in AS-ALD and provides guidelines for the design of SMIs.

AS-TuP-8 Substrate-Driven Selectivity in Area-Selective Atomic Layer Deposition of ZnO: A Theoretical Investigation*, Semin Kim, Yeseul Son, **Taeyoung Kim**, Soo-Hyun Kim, Byungjo Kim,* UNIST, Republic of Korea

As semiconductor devices continue to scale down while demanding higher performance, precise process control and a fundamental understanding of atomic-scale surface reactions become essential. Area-Selective Atomic Layer Deposition (ASALD) has emerged as a promising technique, enabling material growth in designated regions by leveraging surface chemical properties. Unlike conventional ALD, ASALD eliminates the need for additional patterning steps, inherently achieving selective deposition at the nanoscale. This makes ASALD particularly relevant for next-generation semiconductor devices, where precise material placement is critical, such as in 3D-integrated circuits and functional thin-film applications.

Zinc oxide (ZnO), a transparent conductive oxide, has garnered significant interest due to its excellent electrical and optical properties. It is widely used in next-generation semiconductor devices, transparent electrodes, optoelectronic components, and gas sensors. While previous studies on ZnO ASALD have primarily focused on inhibitor-based selective deposition, the influence of inherent substrate properties on ZnO film growth and incubation cycles remains largely unexplored.

In this study, Density Functional Theory (DFT) and molecular dynamics (MD) simulations were conducted to examine how different substrate compositions (SiO_2, Ti, Cu, and Ru) influence ZnO ALD precursor adsorption. To better capture realistic surface configurations, a machine learning force field (MLFF) was implemented, enabling MD simulations that more accurately reflect atomic interactions. Additionally, extensive DFT calculations were performed to quantify the intricate interactions occurring at different surfaces. The analysis revealed substantial variations in precursor-surface interactions, including significant differences in adsorption energies during physisorption. Furthermore, discrepancies in ligand exchange reaction energies were observed, leading to notable shifts in ZnO growth kinetics depending on the substrate. These differences directly impacted incubation cycles, providing a theoretical foundation for substrate-driven selectivity in ZnO ASALD.

By leveraging these insights, we establish a theoretical framework for understanding how chemical reactants interact with different surfaces and how substrate characteristics can be intentionally modified to induce inherent selectivity. This work highlights the importance of a strong theoretical foundation in optimizing atomic layer processing for unprecedented selectivity, offering a pathway to precise pattern control in advanced semiconductor manufacturing.

AS-TuP-9 Inherent Area-Selective Atomic Layer Deposition of Molybdenum Carbide for Bottom-up Semiconductor Manufacturing*, Jeong Hwan Han, **Min Seok Kim**, Ji Sang Ahn,* Seoul National University of Science and Technology, Republic of Korea

With the increasing demand for higher integration and enhanced performance in semiconductor devices, area-selectiveatomic layer deposition (AS-ALD) is playing a crucial role. AS-ALD is a technology that can precisely depositnanometer-level thin films in desired areas, effectively addressing issues that may arise during unnecessary pattern formation or processing. Particularly, selective deposition of metal materials in metallization, and further advanced packaging, where multiple layers of metal need to be deposited sequentially, has the advantage of implementing more complicated structures. Molybdenum carbide (MoC_x) is gaining attention as a promising material for the next generation semiconductor manufacturing due to its excellent mechanical and electrical properties as well as high thermal and chemical stability, there are few reports on Mo-based materialsfor AS-ALD.

In this study, we developed molybdenum carbide (MoC_x) thermalALD using a novel combination ofMo precursor and co-reactant, and conducted analysis of the film properties. Notably, itwas observed that the film growth behavior varied depending on the substrates by analyzing Mo areal density and film thickness. MoC_x films growth was effectively suppressed on Al_2O_3 substrate, whereas significant film deposition was observed on Cu substrate. Despite being a dielectric substrate, the SiO_2 substrate showed similar growth behavior to Cu, suggesting these processes preferred to suppress MoC_x deposition on Al_2O_3. The MoC_x process achieved ~10.4 nm selective deposition on Cu over Al_2O_3 (94.2 % selectivity) and ~13.9 nm on SiO_2 over Al_2O_3 (92.8 % selectivity).These findings demonstrate the feasibility of selective deposition on different substrates, particularly with Al_2O_3 as non-growth area (NGA). This study aims to present an effective approach to overcome technical limitations in next-generation device manufacturing by proposing a method for ASD not only in metal-dielectricapplications but also between dielectrics through theinherentAS-ALD process of molybdenum carbide.

Acknowledgements

This work was supported by Samsung Electronics, and supported by the Technology Innovation Program(RS-2024-00509266, Development of Next-generation dielectric and electrode process equipment for logic 1nm or less and memory xnm level) funded By the Ministry of Trade Industry & Energy(MOTIE, Korea)

AS-TuP-10 Photo-Assisted Atomic Layer Deposition of Metallic Nickel*, **Yupu Tang**, Ion Lambrou, Ville Jokinen, Ville Miikkulainen,* Aalto University, Finland

Photo-assisted atomic layer deposition (Photo-ALD) provides a fundamentally new approach for inherently selective thin film growth, leveraging photo-induced activation rather than traditional surface activation or deactivation methods. In this work, we demonstrate that Ni Photo-ALD achieves selective deposition on a broad range of semiconducting metal oxide substrates, while completely suppressing growth on insulating surfaces—a improvement over previously reported Cu-based processes, which were limited to grow on fewer substrates. The unique optical and chemical interaction between photo, the precursor, and the semiconducting surfaces allows for selective activation, enabling Ni selective growth without the need for external inhibitors or complex patterning steps. This work not only demonstrates the versatility of Ni Photo-ALD across diverse oxide substrates but also highlights its potential as a scalable technique for selective material growth in advanced fabrication processes.

AS-TuP-12 Impurity-Free Accelerators in Atomic Layer Deposition: Driving the Growth of Low-Resistivity Ultrathin Iridium Films, *Se-Hun Kwon, **Myung-Jin Jung**,* Pusan National University, Republic of Korea

Iridium (Ir) has a low figure of merit ($\rho_0 \times \lambda$) and a high melting temperature, so it has recently been spotlighted as a very important copper (Cu) alternative interconnect material in next-generation semiconductor devices. In particular, atomic layer deposition (ALD) enables the deposition of ultra-thin, conformal, and uniform films with excellent step coverage, even in highly complex or narrow trench structures of several-nm dimensions, due to its inherent self-limiting characteristic. In this regard, ALD-Ir is considered one of the most suitable metallization processes for advanced semiconductor interconnect applications.

To develop a reliable ALD-Ir process with improved film quality, considerable efforts have been made. Recently, an ALD-Ir process exhibiting low electrical resistivity and negligible oxygen impurities was reported using Tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$ or TICP) precursor and oxygen [1]. However, despite these advantages, this TICP precursor exhibits a long incubation period and high nucleation delay, making it difficult to deposit extremely thin and continuous Ir films on the hydroxyl-terminated oxide surface.

Therefore, in this study, a method for depositing highly uniform and continuous ALD-Ir thin films with low resistivity even on oxide materials was explored by significantly reducing the incubation period and promoting nucleation through impurity-free accelerators under simple process conditions. This additional step does not change the existing device structure while enabling the formation of high-quality Ir thin films with strong resistance to external impurities. Furthermore, we systematically compared and analyzed the nucleation and growth behavior, as well as film properties, of ALD-Ir on the oxide surface under process conditions with and without the accelerator. As a result, we successfully obtained ultrathin ALD-Ir films with superior uniformity, low surface roughness, and low resistivity, even on oxide surfaces.

References

1. Park, Na-Yeon, et al. Chemistry of Materials 34.4 (2022): 1533-1543.

AS-TuP-13 Area-Selective Atomic Layer Deposition of High-K Dielectric Oxides on Self-Assembled Monolayer Functionalized Nitride Substrates, ***Ting-I Wu**, Shih-Hao Tseng,* Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; Thanh Danh La Duc,* Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Viet Nam*; Yu-Chuan Lin, Hong-Cheu Lin, Yung-Jung Hsu,* Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwan

As semiconductor devices shrink, advanced bottom-up manufacturing techniques are required to fabricate nano-scale electric devices efficiently. To prevent the misalignment encountered in conventional patterning, area-selective atomic layer deposition (AS-ALD) could serve as a promising solution in the semiconductor industry. In this work, we discuss the utility of self-assembled monolayers (SAMs) on nitride substrates, such as SiN or TiN. Benzaldehydes and their functionally derivative groups were used to explore the blocking effects of SAMs utilizing their chemically inert functional groups and carbon chains in various length. Through a variety of surface measurements including water contact angle (WCA), Fourier-transform Infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), scanning probe microscopy (SPM), we verified bonding, coverage, and uniformity of our chosen SAMs on nitrides. Next, SAM-coated nitrides will be used as the substrates to grow AlO_x films via ALD to investigate the blocking effect of the chosen SAMs and correlate their ALD selectivity with SAM thermal stability and SAM surface coverage on nitrides. These results could help advance the manufacturing and scaling of next generation nanoelectronics.

AS-TuP-14 Stabilization of Metal Coated Silicon Photocathodes for Light Assisted CO2 Conversion by Area Selective-Atomic Layer Deposition, *Encarnacion Torralba Penalver, Harsh Chaliyawala, Nikola Ilic,* CNRS-ICMPE, France*; Damien Coutancier,* CNRS-IPVF, France*; Stephane Bastide, Kadiatou Bah, Christine Cachet-Vivier,* CNRS-ICMPE, France*; Negar Naghavi, **Nathanaelle Schneider**,* CNRS-IPVF, France

Photoelectrochemical CO_2 reduction (PEC-CO_2RR) is a promising approach for producing sustainable fuels and chemicals. While many semiconductors have been investigated, silicon-based electrodes modified with metal nanoparticles (NPs) remain underutilized, despite their potential for scalable and cost-effective applications. Among metal catalysts, **copper (Cu) NPs** are widely studied for their ability to generate hydrocarbons and oxygenates. However, their **instability** under reaction conditions—including aggregation, detachment, and dissolution—leads to loss of activity and altered selectivity. These issues are exacerbated under PEC-CO_2RR conditions due to combined light-induced and electrochemical stress, as well as the low catalyst loadings required for efficient light absorption.

Alloying Cu with other metals like Ag or Pd can improve stability, though the effect depends on alloy composition, synthesis, and operating conditions. We recently demonstrated that **Metal-Assisted Chemical Etching (MACE)** is an effective and low-cost method for depositing **bimetallic NPs** (e.g., AgCu, PdCu) on p-Si supports, yielding promising performance in terms of current density and selectivity. However, **Cu-rich systems still degrade rapidly**, highlighting the need for additional stabilization strategies such as **protective coatings** or **nanostructuring**.

In this work, we investigate a novel stabilization method using **Area-Selective Atomic Layer Deposition (AS-ALD)** to coat silicon-based photocathodes with functional oxide layers. AS-ALD leverages the **chemical reactivity contrast** between SiO_2 and metal surfaces, enabling selective deposition of **Al_2O_3** onto the silicon substrate while leaving metal NP surfaces largely uncovered. By tuning precursor chemistry, deposition temperature, and cycle number, we developed **nanometer-thick Al_2O_3 coatings** that protect the substrate without blocking catalytic sites.

Initial PEC-CO_2RR tests of protected electrodes (Ag, Cu, and AgCu NPs on p-Si) show **enhanced NP stability** and **reduced hydrogen evolution**, likely due to decreased exposure of bare Si to the electrolyte. Characterization via XPS, SEM, and PEC measurements confirms partial preservation of the catalyst structure. Some degradation still occurs, likely due to Al_2O_3 porosity. Ongoing work focuses on improving the robustness of the ALD coatings to further enhance long-term durability.

AS-TuP-16 Photocatalytic Surface Initiation for Area-Selective Deposition of Polymer Thin Films and Sustainable Nanomanufacturing, ***Yuanhao Shen**, Xinlei He, Xiaocheng Huang, Pengzhe Cai, Delong Liu, Junjie Zhao,* Zhejiang University, China

Non-lithographic patterning of polymer thin films enables facile fabrication of nanostructures and devices for applications spanning from soft electronics to biomedical engineering. Developing area-selective deposition (ASD) for polymers could achieve self-aligned polymer growth, fostering the generation of complex structures and device configurations with enhanced precision and versatility. However, due to the rapid radical propagation in chain reactions, achieving area-selective radical polymerization in all-dry processes still represents a huge challenge. For conventional initiated chemical vapor deposition (iCVD) and photo-initiated chemical vapor deposition (PiCVD), free radicals are primarily generated in the vapor phase, which leads to uniform deposition with negligible selectivity on different surfaces.

Here, we report a photocatalytic strategy to achieve surface-specific radical generation for polymer ASD. Because radicals are generated by the reaction between photogenerated holes and monomers, photocatalytic surface-initiated chemical vapor deposition (PS-iCVD) not only eliminates the need for initiator, but also can localize radical generation on the photoactive surfaces, which enables ASD of polymer thin films. Moreover, for semiconductors with narrow bandgaps, such as native oxide of Fe, the PS-iCVD can also enable polymer ASD under visible light for fabricating self-aligned patterns with high area-selectivity (97.4% at deposition thicknesses more than 40 nm). The PS-iCVD offers placement control over chain-growth polymers, providing insights for guiding the design of eco-friendly deposition methods and bottom-up non-lithographic nanofabrication. These polymer patterns shown in this work are expected to serve as inhibitors and templates for achieving area-selective atomic layer deposition.

AS-TuP-17 Atomistic Modeling of Selective SiO_2Deposition: Inhibiting Si_3N_4 with Benzaldehyde, ***Seungwon Shim**, Byung Chan Lee, Youngho Kang,* Incheon National University, Republic of Korea*; Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) has emerged as a crucial technique for fabricating semiconductor devices, addressing the limitations of conventional top-down patterning methods based on photolithography. In particular, AS-ALD of SiO_2 on SiO_2 surfaces over SiO_2/Si_3N_4 patterns is considered essential for manufacturing charge trap layers (CTLs) in highly scaled 3D NAND devices with high aspect ratios and reduced ONO tier dimensions. Among various approaches to SiO_2 AS-ALD, the use of small-molecule inhibitors (SMIs) to passivate Si_3N_4 surfaces shows significant promise due to its effectiveness and minimal side effects. For successful implementation of SMI-based AS-ALD, a thorough understanding of the physical and chemical processes involved during film deposition is critical.

In this study, we theoretically investigate SiO_2 AS-ALD on a SiO_2/Si_3N_4 pattern using benzaldehyde (BAD) as a SMI, using density functional theory (DFT) calculations. We first examine the adsorption behavior of BAD on both Si_3N_4 and SiO_2 surfaces to confirm its preferential binding to Si_3N_4. Next, we analyze the reaction between BAD adsorbed on Si_3N_4 and ozone (O_3), a commonly used oxidant in ALD processes, to understand how BAD loses its blocking functionality under oxidative conditions. We also study the potential for BAD re-adsorption on Si_3N_4 following oxidation, evaluating whether repeated inhibitor dosing restores its blocking capability during AS-ALD cycles.

Our DFT results show that BAD selectively adsorbs onto Si_3N_4 surfaces, effectively inhibiting precursor deposition. However, exposure to ozone degrades BAD, resulting in a loss of its blocking performance. Notably, the blocking property is recoverable through repeated BAD dosing, provided the Si_3N_4 surface is only partially oxidized. Once the surface becomes fully oxidized and terminated with –OH groups, re-adsorption becomes significantly hindered.

Overall, our findings demonstrate that BAD serves as a promising inhibitor for SiO_2 AS-ALD due to its selective adsorption on Si_3N_4. Although ozone exposure degrades BAD, its blocking function is restorable through timely re-dosing. These results highlight the importance of controlling re-exposure timing in cyclic AS-ALD processes to maintain selective deposition.

Author Index

Bold page numbers indicate presenter