Area Selective ALD
Room Tamna Hall A - Session AS-TuA
Area Selective Deposition I

Moderators: Stacey Bent, Stanford University, **Mikko Ritala**, University of Helsinki

4:00pm **AS-TuA-11 Surface Chemistry Characterization for Area-Selective Atomic Layer Deposition of Ruthenium***, **Eun-Hyoung Cho**,* 2D Device TU(SAIT)/Samsung Electronics, Republic of Korea*; Young Min Lee, Yunseong Lee, Youngchul Leem, Giyoung Jo, Jeong Yub Lee, Kyung-Eun Byun, Jung Yeon Won, Bongsu Kim, Byeong Gyu Chae,* Samsung Advanced Institute of Technology, Republic of Korea*; Kyeongmin Min, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Iaan Cho, Myeong Kyun Nam, Bonggeun Shong,* Hongik University, Republic of Korea **INVITED**

Achieving atomic-scale precise control over material layering is critical for the development of future semiconductor technology. Area-selective deposition (ASD) has emerged as an indispensable tool for crafting semiconductor components and structures via bottom-up pattern transfer. The most widely used approach for ASD relies on self-assembled monolayers (SAMs) to deactivate specific surfaces. However, alternative strategies are being explored to better align with the requirements of high-volume device manufacturing and address the limitations of the SAM method. One promising alternative involves the application of small molecule inhibitors (SMIs). However, limited research has been conducted to elucidate the mechanisms governing their adsorption and inhibition of deposition. Additionally, research on elucidating the ASD mechanism, in which precursors are blocked rather than chemically adsorbed on SMIs, has predominantly relied on simulations such as density functional theory (DFT) calculations or Monte Carlo (MC) simulations. By closely investigating these interfacial phenomena using precise surface analysis techniques, a deeper understanding of the role that SMI composition and structure play in adsorption and inhibition can be achieved, ultimately contributing to the design of SMIs for future ASD systems. Recently, it was confirmed that by controlling the crystal orientation of metal grains, atomic layer deposited ruthenium (Ru) thin films on amorphous dielectric substrates exhibit electrical resistivity comparable to that of single crystal Ru. However, the oxidative counter-reactants such as O2 often used for atomic layer deposition (ALD) of metallic Ru films result in a considerable increase in contact resistance because of substrate oxidation, limiting the applications of both ALD and ASD of Ru. In this study, Ru ASD is demonstrated using two-step ALD with the sequential use of H2 and O2 as counter-reactants and dimethylamino-trimethylsilane (DMATMS) as a precursor inhibitor. Both theoretical and experimental results demonstrate that in the two-step Ru ALD, the oxide layer can be eliminated via the reduction of the oxidized substrate metal surface by the H2 counter-reactant. This mechanism simultaneously facilitates the adsorption of the Ru precursor (tricarbonyl-(trimethylenemethane)-ruthenium) and removal of the surface oxide layer. Consequently, Ru growth is suppressed on the DMATMS-inhibited SiO2 surface during ASD, enabling exclusive deposition of Ru on the Mo surface. The currently proposed Ru ASD scheme using two-step ALD is highly promising for driving advancements in interconnect technology for commercial applications.

4:30pm **AS-TuA-13 Area-Selective Solid-State Synthesis of Nickel Silicide Nanostructures***, **Gabriele Botta**,* Nanogune, Italy*; Mato Knez,* nanogune, Croatia

Over the past decade, metal silicides have been re-discovered for their significant potential across various fields of nanotechnology. [1,2,3] However, integrating them into modern devices continues to pose challenges, primarily due to limited control over phase formation during their synthesis. [4] Additionally, since they are typically grown as continuous layers, their structuring often relies on complex top-down patterning techniques, which significantly limit their practical applications. [5] This study addresses these issues by proposing a method for Area-Selective (AS) silicidation (Fig. 1a SD). Our approach ensures that during material synthesis, the resulting silicide nanostructures acquire a predefined morphology and nucleate exclusively in the targeted regions of the substrate.

The AS silicidation process is demonstrated through the formation of NiSi$_2$ structures on Si(100) and Si(111) substrates (Fig. 1b SD), and its broader applicability is further illustrated with the successful AS synthesis of Cu$_3$Si (Fig. 1c SD). To direct growth, the silicon substrates are patterned using ion beams, which create surface defects that promote silicide nucleation in the desired areas. Unlike conventional Solid State (SS) synthesis, which involves annealing a metal thin film on silicon, our method begins with an ALD deposited metal oxide. Silicidation is performed by annealing in the presence of a reductant (H$_2$), which reduces the metal oxide to its metallic state. The resulting metal then reacts with the underlying silicon, forming a metal silicide. During this two-step reaction, the material re-arranges along surface defects, which act as templates, guiding both the shape and positioning of the forming silicide crystals.

The effectiveness of this multi-step fabrication method, coupled with its adaptability to various metal-silicide systems, underscores its potential to create functional, structured silicides without the need for post-synthesis nanopatterning.

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4:45pm **AS-TuA-14 ALD Outstanding Presentation Award Finalist: High Temperature Area Selective ALD SiN by in-Situ Selective Surface Fluorination***, **Haonan Liu**, Ken Okoshi, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd., Japan

Presently, research on area selective atomic layer deposition (AS-ALD) is attracting strong interest. AS-ALD simplifies the process of deposition on patterned substrates and high aspect ratio (AR>70) structures, holding promise for various applications in semiconductor manufacturing. Inhibitors such as self-assembled monolayers (SAMs) and (dimethylamino)trimethylsilane (DMA-TMS) are typically used to passivate non-growth areas.[1] However, the deterioration of selectivity at temperatures exceeding 500℃ limits their applications in high temperature deposition processes. Fluorination is regarded as a candidate for overcoming these problems.[2] In this study, we present a novel approach to achieve high selectivity in high temperature AS-ALD on SiN versus SiO$_2$ through effective surface-selective fluorination without damage to the substrates.

Experiments were conducted with a batch furnace capable of treating over one hundred 300 mm wafers simultaneously. A wide range of substrates were utilized including 300mm wafers with blanket SiN and SiO$_2$ films and various nanostructured samples. Prior to inhibition, samples were precleaned by dilute HF to remove native oxides. An HF gas passivation was employed at 630℃ for 10 minutes to selectively inhibit the SiO$_2$ surface. ALD SiN was deposited with dichlorosilane (SiH$_2$Cl$_2$) as the precursor and NH$_3$ as the co-reactant at 630 ℃.

The initial AS-ALD sequence involved performing ALD cycles following HF passivation, resulting in AS-ALD of up to 6 nm SiN on SiN while maintaining good within-wafer non-uniformity (Win Unif.) of <3%. We then developed the area-selective-deposition-Loop (ASD-Loop) technique, consisting of alternating 10-minute HF passivation with ALD cycles, as shown in Figure 1. We achieved an AS-ALD of 28 nm on SiN blanket wafers with high selectivity while keeping excellent Win Unif. of <2% and high film quality, as confirmed by the wet etching rate. The ASD-Loop has also been successfully applied to SiN/SiO stripe-patterned substrates (Figure 2), resulting in a maximum ASD thickness of 21 nm; and to high-AR holes on SiO$_2$/SiN stacks (Figure 3), resulting in AS-ALD with high conformality of >90%. Thus, we have demonstrated high-temperature AS-ALD on 300 mm wafers and complex nanostructures with high selectivity, superior uniformity, and reliable quality. This offers a new pathway for the integration of AS-ALD into nanofabrication schemes, showing significant potential for advancing high-performance semiconductor applications including DRAM and 3D NAND manufacturing.

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5:00pm **AS-TuA-15 Mutifunctional Ru/ZnO Bilayer for Sustainable Cu Interconnects using Area-Selective Atomic Layer Deposition of barrier with Small Molecule Inhibitor***, **Minwoo Kim,** Yeseul Son, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

With the scaling of semiconductor devices, the increase in via resistance, which constitutes a significant portion of the Cu interconnect resistance, has emerged as a critical issue. To reduce via resistance, studies [1, 2] have been conducted on forming bottomless barriers using area selective deposition (ASD), where a high-resistivity barrier layer is selectively deposited only on the via/trench sidewalls, SiO_2-based dielectrics without being deposited on the via bottom, Cu. In these studies, self-assembled monolayers (SAMs) with long alkyl chains were used as inhibitors for preventing the adsorption of the precursor on metallic surfaces. However, SAMs are typically adsorbed onto surfaces through solution-based processes, which pose compatibility issues with semiconductor processes and, due to their relatively long molecular structure, cannot form a uniform inhibitor layer within 3D nanostructures. To prevent these issues, this study used a small molecule inhibitor (SMI) to form a bottomless barrier. Additionally, based on previously reported studies [1], the Ru/ZnO bilayer, with ZnO for the bottomless barrier and Ru for the liner and seed layer, was applied for the sustainable Cu interconnects [Figure 1]. The ZnO ASD process is carried out using an amine-based SMI that selectively absorbs on Cu, with diethylzinc and H_2O used for the ZnO ALD process. After the ZnO ASD process and the removal of the inhibitor, the Ru film was deposited using an ALD process with tricarbonyl(trimethylenemethane)ruthenium and O_2. By controlling the conditions of the ZnO ASD process, we confirmed and analyzed the selective deposition of ZnO on the SiO_2-based dielectric substrate not on Cu one using TEM, XPS, and XRD etc. The detailed results will be presented in the conference.

References

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Acknowledgements

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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.

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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

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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)(η^5-C_7H_7O)(η^5-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

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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

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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.

Area Selective ALD
Room Tamna Hall A - Session AS1-WeM
Area Selective Deposition II

Moderators: Anjana Devi, Leibniz Institute, IFW Dresden, **Il-Kwon Oh**, Ajou University

8:00am **AS1-WeM-1 Area-selective ALD of ZnS on Atomic Layer Etched (ALE) Substrates via Growth Modulation*, Taewook Nam,*** Sejong University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) has become essential for advanced semiconductor manufacturing by enabling precise bottom-up material deposition and reducing process complexity. Various approaches have been developed to achieve selective deposition, including surface activation, growth inhibition using self-assembled monolayers, and growth-etch back processes. These strategies are particularly crucial for fabricating self-aligned features in advanced technology nodes, where traditional lithography and etching face increasing challenges in meeting the demands of device scaling.

Thermal atomic layer etching (ALE) is a method for thin film removal based on sequential surface modification and volatile release reactions. After thermal ALE, atomic layer deposition (ALD) may be needed to deposit another material on the etched surface. Many thermal ALE procedures are defined by sequential fluorination and ligand-exchange reactions. These reactions can leave the surface terminated with fluoride and methyl or chloride species, respectively. These terminated surfaces may inhibit ALD. Additional chemical treatment may be required to reactivate the surface for normal ALD growth.

In this study, zinc sulfide (ZnS) ALD was conducted on Al_2O_3, SiO_2, HfO_2, and native oxide on Si substrates before and after ALE. The ALE was performed at 300 °C using sequential HF and $Al(CH_3)_3$ (TMA) exposures. ZnS ALD was conducted at 300 °C using diethylzinc (DEZ) and hydrogen sulfide (H_2S) exposures. The ZnS ALD thicknesses were monitored using in situ spectroscopic ellipsometry. When ZnS ALD was performed on as-deposited Al_2O_3 ALD films, the ZnS ALD films grew immediately with no noticeable nucleation delay. In contrast, the ZnS ALD growth was completely inhibited until 50 ALD cycles after the Al_2O_3 film was etched using sequential HF and TMA exposures. Similar results were observed for the other metal oxide substrates.

Various chemical treatments were explored to reactivate the metal oxides after ALE for normal ZnS ALD. The surface species present after ALE using HF and TMA exposures are fluoride or methyl species. These species lead to a nucleation delay for ZnS ALD. These surface species can react with exposures of H_2O_2 or H_2O to add hydroxyl groups to the surface. The ZnS ALD had only a slight nucleation delay using H_2O_2 exposures after ALE. This study reveals that ZnS ALD growth occurred almost immediately after H_2O_2 reactivation of the etched Al_2O_3 substrate. Results will also be shown for different chemical treatments for the various metal oxide substrates.

8:30am **AS1-WeM-3 Passivation of Nitride Surface Using Aldehyde Inhibitor for Area Selective Atomic Layer Deposition of SiNx on Oxide Surface*, Summal Zoha,*** *Ngoc Le Trinh, Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

In recent years, area-selective atomic layer deposition (AS-ALD) has emerged as a superior technique for precise and selective thin-film deposition, surpassing conventional methods. AS-ALD has demonstrated promising potential for 2D and 3D nanoscale patterning by using inhibitor molecules to tailor surface properties. This approach enables thin-film deposition exclusively on desired growth surfaces (GS) while preventing unwanted growth on non-growth surfaces (NGS). Among various inhibitors, small molecule inhibitors (SMIs) have received significant attention for their effective inhibition despite their small size. The choice of surface inhibitor is crucial in determining the selectivity between growth and non-growth surfaces, as well as the degree of surface passivation. In this study, an aldehyde-based inhibitor, trimethylhexanal (TMH), was utilized for AS-ALD to achieve selectivity between oxide and nitride surfaces. TMH displayed selective adsorption on a diluted hydrofluoric (DHF) acid-treated Si_3N_4 surface while leaving the SiO_2 surface unaffected. The DHF pretreatment facilitated favorable TMH adsorption on Si_3N_4 via interactions with NH and NH_2 surface groups, whereas the OH-terminated SiO_2 surface exhibited no TMH adsorption. Density functional theory (DFT) calculations confirmed the favorable adsorption energy of TMH on the nitride surface. To assess the blocking properties of TMH, SiN_x ALD was performed using silicon tetrachloride ($SiCl_4$) as the precursor and ammonia (NH_3) as the reactant. The results demonstrated that SiN_x could be selectively deposited on the SiO_2 surface with no detectable growth on the TMH-treated Si_3N_4 surface. This process shows great promise for 3D patterning in silicon devices, where AS-ALD is critical to meeting the demands of miniaturization.

8:45am **AS1-WeM-4 Blocking Effects of Small Molecule Inhibitors in Atomic Layer Deposition: An Off-lattice Kinetic Monte Carlo Study*, Zhaojie Wang,*** *Yanwei Wen, Rong Chen, Bin Shan,* Huazhong University of Science and Technology, China

Small molecule inhibitors (SMIs) hold great promise for their compatibility with area-selective atomic layer deposition (AS-ALD) due to their gas-phase dosing scheme. However, it is quite challenging to describe the complex steric hindrance of inhibitors in simulations. In this work, an off-lattice kinetic Monte Carlo (KMC) simulation method is developed to evaluate the performance of SMIs. The heat-driven conformation transformations are considered in our method. During our simulation, the shape of each molecule is constantly changing to describe its dynamic steric hindrance, which is achieved by constantly refreshing its conformation following the Boltzmann distribution. The results show that the saturated deposition density of long-chain thiol inhibitor 1-mercapto octane on the substrate (~1.4/nm^2) is relatively lower than ethanethiol (~2.0/nm^2) due to its larger size, and the branched isomer 2-Ethyl-1-hexanethiol has an even lower deposition density (~1.1/nm^2). When DMAI is used as an ALD precursor, 1-mercapto octane has a better blocking effect than shorter thiol inhibitors despite its lower deposition density, which emphasizes the large steric hindrance provided by the long chain. Benzene-containing inhibitors show better DMAI-blocking performance than thiols due to their stronger binding strength to the substrate. Meanwhile, the desorption of SMIs gets faster after the simulation temperature increases from 100 to 130°C, resulting in a more rapid blocking failure. This work provides a reasonable method to study the molecular steric hindrance of SMIs and can be applied to large-scale molecular screening of potential inhibitors.

9:00am **AS1-WeM-5 Controlling the Surface Chemistry of Silicon Nitride Using a Plasma Pretreatment for Area-Selective Deposition*, Marc Merkx,*** *Pengmei Yu,* Eindhoven University of Technology, Netherlands*; Jhon González,* Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin,* eindhoven University of Technology, Netherlands*; Rachel Nye de Casto, Dennis Hausmann,* Lam Research Corporation*; Erwin Kessels,* Eindhoven University of Technology, Netherlands*; Tania Sandoval,* Universidad tecnica Federico Santa Maria, Chile*; Adriaan Mackus,* eindhoven University of Technology, Netherlands

Selective deposition on SiO_2/SiN_x patterns, where either oxide-on-oxide or nitride-on-nitride deposition is desired, is currently considered as the “holy grail” in the field on area-selective deposition (ASD). Unlike other silicon-based materials (e.g., Si, SiO_2), SiN_x can be terminated with a large variety of surface groups e.g., (NH_2, NH, N, SiH). As a result, the surface chemistry of a SiN_x surface is very sensitive to the manner in which the layer was deposited, and to how the layer was treated after deposition. In addition, in case of air exposure, this surface chemistry becomes even more complex due to (partial) oxidation of the layer (which adds OH groups). For ASD, the surface chemistry of the SiN_x strongly affects the (selective) adsorption of the inhibitors and precursors. In this contribution, it will be discussed how plasma pretreatments can be used to control the surface chemistry of a SiN_x surface and correct for any unwanted oxidation, as well as how the obtained surface chemistries affect inhibitor adsorption on a SiN_x surface.

Three different plasma chemistries were explored: N_2, H_2, and NH_3 plasma. In-situ reflection adsorption infrared spectroscopy (RAIRS) results show that the N_2 and NH_3 plasma pretreatments were effective in removing the OH groups introduced by air exposure, whereas the H_2 plasma was insufficient and only partially removed the OH groups. The N_2 plasma was observed to result in a largely N-terminated SiN_x surface, while the NH_3 plasma resulted in a largely NH_2-terminated surface. The effect of the plasma pre-treatments on the adsorption of trimethylacetaldehyde (TMAAH) and acetylacetone (Hacac) inhibitor molecules onto the SiN_x was studied using in-situ RAIRS and density functional theory (DFT) calculations. Our results show that the SiN_x surface termination strongly affects whether and how strongly the inhibitors adsorb on the SiN_x surface. Importantly, Hacac was found to require a N-terminated SiN_x surface for adsorption, while TMAAH adsorbs most strongly on a NH_2-terminated surface. Therefore, these results demonstrate the importance of understanding and controlling the surface chemistry for ASD.

9:15am **AS1-WeM-6 Enhancing Area Selective Deposition Through Sub-saturated ALD: A Pathway to High Volume Manufacturing***, **Nupur Bihari**,* Lam Research Corporation

Area Selective Deposition is a key technique in semiconductor fabrication processes, enabling the deposition of thin films in a controlled, pattern specific manner. Achieving a high level of selectivity, i.e., no growth on "non-growth surface" and high-density continuous growth on the "growth surface" is essential for ensuring good device yield. Traditional Atomic Layer Deposition processes often face limitations in selectivity due to the inherent challenges in controlling surface chemistry and reaction kinetics.

This talk will explore an approach to enhancing area selectivity through a subsaturated ALD process. By carefully controlling the precursor selection, flux and reaction time to operate in a subsaturated regime, we can significantly reduce unwanted deposition on non-target areas while ensuring high quality film growth on desired regions. This method leverages the intrinsic self-limiting nature of ALD while mitigating issues such as precursor overexposure and undesired nucleation, resulting in improved spatial uniformity and deposition control.

The talk will present experimental results demonstrating the superior selectivity and film quality achieved with sub-saturated aluminum oxide ALD in a dielectric on dielectric (DoD) process compared to a traditional, saturated process. We will also discuss the underlying mechanistic insights, including the role of surface coverage, precursor dynamics and impact of process parameters such as temperature, dilution and pressure. Additionally, a known challenge with ASD – metrology will be discussed. Lam's successful attempts at image processing to understand large scale selectivity over an entire die will be presented. With the need to shorten the time from R&D to High Volume Manufacturing (HVM), this fast, quantitative metrology is key to rapid validation of new processes.The quick turnaround image processing method allows for testing of marginal processes enabling a larger number of experiments in a short period of time.

This work provides future directions for optimizing selectivity and process uniformity at smaller pitches across a wide range of semiconductor applications.

9:30am **AS1-WeM-7 Inherent Area-Selective Deposition of Low-Resistivity Molybdenum Carbide Films by Thermal Atomic Layer Deposition***, Jeong Hwan Han, **Ji Sang Ahn**,* Seoul National University of Science and Technology, Republic of Korea

With the ongoing downscaling of logic and memory devices, one of the main challenges has emerged such as edge placement error issues resulting from top-down patterning. To overcome the limitations of lithography, a recent focus in bottom-up patterning is based on area-selective atomic layer deposition (AS-ALD). Numerous studies have investigated AS-ALD that employed precursor inhibitors such as SAMs or SMIs to prevent precursor adsorption in non-growth areas. However, there is an increasing need for research into inherent AS-ALD strategies, which exploit the intrinsic properties of substrates with the chemical adsorption of the precursor to enable selective adsorption at targeted surface sites. Molybdenum carbide (MoC_x) has attracted as promising materials for metallization, particularly as bottomless diffusion barriers, liners, capping layers, and interconnects, due to their high melting points, low resistivity, excellent thermal stability, and low reactivity with Cu and its area selective deposition methods have been requiring.

In this work, we developed conductive MoC_x films via thermal ALD without the use of halogen-based precursors, at the deposition temperatures of 200−300℃. This process enabled area-selective growth of MoC_x films on metallic substrates (TiN, Ru, Cu) over oxide substrates (SiO_2, Al_2O_3) by utilizing the intrinsic chemical adsorption of the precursor. We investigated the crystallinity, chemical bonding states, impurity, and resistivity of the MoC_x films, and evaluated the selectivity between substratesthrough analysis of Mo areal density and film thickness. Moreover, the selective growth of MoC_x films on metallic substrates was demonstrated on metal/dielectric patterns using auger electron spectroscopy (AES) mapping and energy-dispersive X-ray spectroscopy (EDS) analysis, indicating the feasibility of implementing this process in practical device applications. To elucidate substrate-dependent surface chemistry in MoC_x AS-ALD, density functional theory (DFT) calculations were conducted, revealing the relative adsorption energies of Mo precursor between metal and dielectric substrates. In conclusion, a newly developed inherent AS-ALD of MoC_x films presents a promising alternative to top-down processes, offering a simplified workflow and potential conducting materials for advanced metallization.

9:45am **AS1-WeM-8 Molecular Design of ALD Precursors Through Atomic-Level Simulation and Their Reactivity Analysis***, **Yusuke Asano**, Kota Matsumoto, Makoto Sato,* Preferred Computational Chemistry, Japan

Atomic Layer Deposition (ALD) is a process that forms uniform thin films with atomic-level precision. Within this process, Area-Selective Deposition (ASD)—a technique that achieves film growth selectively on specific areas—has garnered significant attention, and recent research has been actively focused on it. With advancements in computational chemistry, the atomic-level mechanisms in ALD processes have been elucidated, enabling the design of ALD processes and ALD precursors using these insights.

In this study, we propose a method for designing ASD-suitable precursor molecules using atomic-level simulations with an universal machine learning interatomic potential (uMLIP). Specifically, we constructed an adsorption energy dataset for various precursor model molecules using adsorption energy calculations for areas where film formation is desired and areas where it is not (modeled as H-terminated Si surfaces and alkyl-protected surfaces, respectively). Through the sparse modeling of this data, we extracted ligand features that enhance adsorption selectivity towards H-terminated Si surfaces and alkyl-protected surfaces. Consequently, we successfully identified ligand candidates that increase adsorption selectivity towards H-terminated Si surfaces.

Furthermore, by combining a uMLIP with the Global Reaction Route Mapping (GRRM) method, we successfully analyzed the ligand dissociation mechanisms of ALD precursor molecules on surfaces. These methods allow for the design of precursor molecules that meet the high adsorption selectivity and ligand dissociation requirements necessary for ASD.

Area Selective ALD
Room Tamna Hall A - Session AS2-WeM

Area Selective Deposition III

Moderators: Rick Chen, The Electronics business of Merck KGaA Darmstadt, **Kivin Im**, SK hynix

10:45am **AS2-WeM-12 Industrial ALD/ASD Perspectives: Atomic Level Process Control for Semiconductor Devices***, **HanJin Lim**,* Samsung Electronics, Republic of Korea **INVITED**

As the semiconductor devices are highly integrated and refined to feature sizes of 10 nm or less, the thickness of the functional films that affect the electrical properties of the device is also thinned to 5 nm or less. Since the role of the interface becomes dominant in such a functional thin film, engineering techniques using various interfacial layers for electrical properties are being introduced. On the other hand, in order to implement such a thin film in a 3D semiconductor structure, ALD technology is essential, and various processes and interfacial layer technology introduction cases are to be examined for phase stabilization and interface control of atomic level film quality. In addition, in order to realize high-quality and uniform film quality in a complex 3D structure, we will look at examples of innovation in ALD precursors and facility technologies and advancement of process technologies, and finally, we will look at cases of improvement in semiconductor device characteristics using selective deposition technology.

11:15am **AS2-WeM-14 Area-Selective Deposition for Dielectric Films on Metal Substrates: Coupon to Full Wafer***, **Rachel Nye de Castro**, Paul Lemaire, Alexander Fox, Joel Smith, Nupur Bihari, Bill Nunn, Kevin Mclaughlin, Dennis Hausmann,* LAM Research

Area-selective deposition (ASD) has potential to reduce reliance on costly lithography steps and improve shorting margins for small pitch sizes. ASD has been successfully demonstrated for many material sets, notably dielectric on dielectric (DoD) for fully self-aligned vias,[1] yet the demand for thicker films and new materials continues to grow to enable advanced applications. Selectively depositing a film on a surface of a different type, e.g. a dielectric film on a metal substrate, is inherently more challenging because after the first few cycles of deposition, both the growth and non-growth surfaces are the same type (dielectric in this example), resulting in similar reactivity towards ALD precursors. This work discusses the development of selective dielectric on metal (DoM) deposition from coupon-scale to full wafer patterns.

We utilize inhibitor molecules to selectively block deposition on our desired non-growth surface (dielectric in this case). Numerous inhibitors are screened on both dielectric (SiO_2, SiON, SiOC, etc) and metal (W, Co, Cu, Ru, etc) surfaces using water contact angle (WCA) measurements to characterize hydrophobicity after selective inhibitor adsorption. Inhibitors with the best WCA contrast between dielectric and metal are then evaluated for blocking performance using AlO_x ALD.Ellipsometry, mass, and x-ray reflectivity measurements demonstrate several nm of AlO_x deposition on metal surfaces without any selectivity loss on dielectric. Further verification from TEM and EELS elemental analysis confirm that this selectivity is extended to patterned coupons and full wafers. We demonstrate selective AlO_x on patterned wafers with excellent selectivity (EELS, top-down SEM), which is also extended to other deposited films (e.g. SiN, MoN). These inhibitors are compatible with high volume manufacturing requirements, 3D features, and a wide range of temperatures that accommodates low thermal budget materials as well as high temperature ALD processes. This selective DoM process enables applications such as selective hard masks and etch stop layers and improved shorting margins.

References

Parsons, G. N.; Clark, R. D. *Chem. Mater.* **2020,** *32,* 4920-4953.

11:30am **AS2-WeM-15 Redox-coupled Inherently Selective Atomic Layer Deposition of SiO_2 on SiO_2/Si_3N_4 for 3D NAND structure***, **Kun Cao**, Zilian Qi, Eryan Gu, Rong Chen,* Huazhong University of Science and Technology, China

Area-selective atomic layer deposition (AS-ALD) provides a promising approach for bottom-up fabrication by enabling atomic-level control over material growth in pre-defined patterns, particularly on complex 3D architectures. In this study, a novel strategy is proposed that combines surface-state modulation via alcohols pre-treatment with oxygen partial pressure optimization to enhance selectivity between SiO_2 and Si_3N_4 surfaces. Methanol pre-treatment maintains the amination of Si_3N_4 surfaces, effectively delaying nucleation in non-growth regions, while controlling oxygen partial pressures prevent undesired oxidation of amines to hydroxyl groups. Di(isopropylamino)silane (DIPAS) is employed as a selective SiO_2 precursor, demonstrating inherent selectivity without additional surface inhibitors. The inclusion of dynamic precursors pulses in the ALD process further improved precursor transport and reaction uniformity in high-aspect-ratio 3D NAND structures. This approach achieved ~3 nm thick SiO_2 films on SiO_2 surfaces, with minimal deposition on Si_3N_4 surfaces. Uniform deposition across the top and bottom layers of high aspect ratio 3D structures is demonstrated. This approach combines methodology of surface-state engineering and dynamic precursor pulsing highlights a robust method for expanding AS-ALD applications in complex 3D nanoelectronics.

11:45am **AS2-WeM-16 Area-selective Atomic Layer Deposition of Ruthenium via Plasma Surface Modification***, In-Hwan Baek, **Dahui Jeon**,* Inha university, Republic of Korea

As semiconductor devices continue to scale down and increase in complexity, achieving both high performance and reliability has become increasingly critical. Ruthenium (Ru) has emerged as a key material for next-generation interconnects and electrode applications due to its low resistivity (~7.1 μΩ·cm), high work function (~4.7 eV), and excellent chemical stability. To fully utilize these properties, area-selective atomic layer deposition (AS-ALD) is essential for enabling Ru deposition exclusively in growth regions while inhibiting it in non-growth areas. This bottom-up patterning approach mitigates edge placement error (EPE) and enhances overall process yield.

Conventional AS-ALD techniques using self-assembled monolayers (SAMs) as surface inhibitors are inherently limited by their low thermal stability, leading to selectivity degradation over multiple cycles. As the deposition process proceeds, SAM desorption or decomposition leads to unwanted Ru nucleation in non-growth regions, compromising the selectivity of the process. Furthermore, achieving uniform SAM coverage in high-aspect-ratio structures poses additional challenges.

To overcome these limitations, we developed an atmospheric-pressure X plasma surface modification process, which introduces hydrophobic functional groups that effectively suppress Ru nucleation in non-growth areas while maintaining stability throughout multiple ALD cycles. This method demonstrated infinite selectivity, with no Ru deposition detected in non-growth regions even after 200 ALD cycles, while achieving over 30 nm of Ru film growth in targeted areas—exceeding the selectivity performance of conventional AS-ALD approaches.

Additionally, we established a substrate-dependent X plasma effect, demonstrating selective removal of hydrophobic X functional groups based on surface chemistry, which influenced Ru nucleation behavior. Furthermore, we verified that post-deposition atmospheric O_2 plasma treatment effectively eliminates residual X inhibitors from non-growth areas without compromising Ru film integrity in growth regions. These findings highlight plasma-assisted AS-ALD as a scalable, highly selective approach for advanced semiconductor integration.

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Area Selective ALD
Room Tamna Hall A - Session AS-WeA

Area Selective Deposition IV

Moderator: Jeffrey W. Elam, Argonne National Laboratory

2:00pm **AS-WeA-3 Area Selective Deposition of $SiAlO_x$ Films for Self-Aligned Dielectric-on-Dielectric Application**, ***Eryan Gu***, *Wang Li, Kun Cao, Rong Chen,* Huazhong University of Science and Technology, China

Area selective deposition (ASD) is a high-precision atomic-level manufacturing technology that enables the development of bottom-up manufacturing methods in the future semiconductor field. As the feature size decreases, the parasitic capacitance increases, and the RC delay limits the propagation speed of the signal, while increasing the power consumption of the chip. This study investigates the $SiAlO_x$ film via atomic layer deposition (ALD) process, focusing on the catalytic reaction mechanisms of various aluminum precursors on silicon. Trimethylaluminum (TMA) molecules, which are highly reactive, easily interact with Bis(ethylmethylamino)silane (BEMAS), resulting in relative lower k value. In contrast, dimethyl isopropylaluminum (DMAI) molecules exhibit lower reactivity, resulting in a slower catalytic reaction rate. Additionally, n-octadecanethiol (ODT) is used to inhibit nucleation on the metal surface, and the interaction between aluminum and silicon precursors and ODT is studied. The high catalytic activity of TMA on BEMAS will decrease selectivity, while the DMAI system can achieve high selectivity with 10nm on growth area of SiO_2 with minimal growth on non-growth area of Cu. This approach not only reduces the k value further but also offers a promising pathway for advancing semiconductor nodes.

References

1. Effect of Al precursor's properties on interactions with self-assembled monolayers for area selective deposition. Eryan Gu, Jin Yan, Boxuan Li, Huilong Zhou, Zhuhui Lu, Yanwei Wen, Kun Cao, Rong Chen, J. Vac. Sci. Technol. A 42, 062403 (2024)

2:15pm **AS-WeA-4 Control of Three-Color Area-Selective Deposition of PEDOT Conjugated Polymer on SiN vs SiO2 and Si-H by Adjustment of Pre-Treatment Sequence**, ***Jeremy Thelven***, *Nicholas Carroll, Gregory Parsons,* North Carolina State University

Most research in area-selective deposition (ASD) focuses on deposition of one material on a growth surface while avoiding deposition on a non-growth surface. However, for many steps in manufacturing, the exposed surface is "multi-color", consisting of three or more materials. This means that any desired ASD process must be tuned to deposit on more than one growth surface while simultaneously inhibiting deposition on more than one non-growth surface.

To analyze "three-color" ASD, we studied ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and CVD using ethylene-dioxythiophene monomer and $SbCl_5$ as reactants for oxidative polymerization.[1–2]As a three-color substrate, we use blanket samples of silicon nitride, silicon dioxide, and silicon.Initially, we treat all three surfaces with dilute HF solution producing Si-NH, Si-OH, and Si-H surface termination, respectively.As shown in Figure 1, PEDOT CVD at 150°C results in "inherent" selectivity of more than 30 nm on SiN and SiO_2, with no substantial deposition on Si-H. This selectivity has been ascribed to Si-H reacting with the $SbCl_5$ oxidant, preventing subsequent monomer oxidation on that surface.

To control selectivity, three surface treatments were explored: 1) one cycle of MoF_6/N_2 gas for 1s/30s, respectively, at 250°C; 2) N,N-dimethylamino-trimethylsilane (DMATMS) vapor for 15 s at 250°C; and 3) DMATMS for 15 s at 250°C followed by liquid water for 15 minutes at room temperature. Figure 1 shows the resulting PEDOT thickness (from ellipsometry) vs deposition time. The MoF_6 vapor had minimal influence on growth on SiN but converted the SiO_2 from growth to non-growth, due to conversion of reactive Si-OH to non-reactive Si-F, while simultaneously converting the Si-H from non-growth to growth, ascribed to the presence of some Mo on the Si-H. Additional control was achieved using DMATMS and liquid water. The DMATMS vapor inhibited deposition on Si-OH but had no effect on Si-H, and minimal effect on SiN, consistent with DMATMS reacting preferentially to consume Si-OH groups to produce a hydrophobic $Si(CH_3)_3$ surface. After DMATMS, we find that exposure to liquid water selectively "actives" the Si-H via surface oxidation, with little change to the DMATMS-modified SiO_2, allowing ASD on SiN and Si-H regions vs SiO_2.

Overall, these results demonstrate the concept of selectivity control for ASD of one material on "multi-color" substrates, thereby providing insight into means to adjust selectivity for a variety of future applications.

1. Kim, J.-S. et al., *Chem. Mater.* **2021**, 33, 23, 9221-9239
2. Carroll, N. M. et al., *Chem. Mater.* **2024**, 36, 8, 3655-3665

2:30pm **AS-WeA-5 Annealing PEDOT Thin Films to Generate a Selectively Deposited Etching Hard Mask Layer**, *Nicholas Carroll, Carwynn Rivera, Man Hou Vong, Hannah Margavio,* North Carolina State University*; Hwan Oh,* Brookhaven National Laboratory*;* ***Gregory Parsons,*** North Carolina State University

As feature sizes in contemporary device architectures aggressively shrink, enhanced understanding of area-selective deposition (ASD) is critical to support advanced patterning and feature alignment. In recent years, new strategies have been developed for ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and chemical vapor deposition (CVD) on SiO_2 vs. Si-H,[1] orthogonal ASD of W and PEDOT,[2] and inverted "dual-tone" ASD of PEDOT on Si-OH vs. SiO_2-TMS.[3]

Hard masks for etching are a key application for ASD materials. However, conjugated polymers are expected to etch quickly during plasma exposure. In this work, we describe the effect of post-deposition annealing on the etch rate of PEDOT during O_2 plasma and demonstrate means to "reactivate" the film to convert it from non-etching to etching. In their as-deposited form, the materials etch readily, as expected. As shown in Figure 1(a), the etch rate decreases by 50% upon annealing at 250 °C and decreases to near zero after heating to 350 °C. XPS analysis in Figure 1(b) shows an increase in the concentration of the Sb oxidant after annealing. Also, Figure 1(c-e) shows HAADF STEM images and an EDS elemental map of a film after annealing 350 °C. The EDS indicates that upon annealing, Sb segregates to the film surface. We hypothesize that this Sb layer contributes to the observed reduction in etch rate. This is consistent with XPS after etching in Figure 1(f) showing Sb present in the film.

Interestingly, we find that after treating the annealed PEDOT in deionized liquid H_2O at 80 °C for 10 minutes, the films readily etch in O_2 plasma, as indicated by XPS in Figure 1(g). The ability to enable plasma etching resistance for a selectively deposited conjugated polymer film opens innovative avenues and strategies for protecting surfaces during plasma deposition or selective etching steps. These findings bolster the significance and versatility of ASD for modern manufacturing methodologies.

[1] J.-S. Kim et al., *Chem. Mater.* **33**, 23 (2021).

[2] H. Oh et al., *Chem. Mater.* **35**, 11 (2023).

[3] N. Carroll et al., *Chem. Mater.* **36**, 8 (2024).

2:45pm **AS-WeA-6 Ring-Opening Enhanced Etching of Cyclosiloxanes for Area-Selective MLD of SiOC(H) Thin Films**, ***Xiaocheng Huang***, *Weiwei Du, Yuanhao Shen, Pengzhe Cai, Delong Liu, Junjie Zhao,* Zhejiang University, China

As the feature sizes of semiconductor devices continue to shrink, edge placement errors caused by the overlay variations in lithography will lead to dramatically increased failure probability and durability issues. Area selective deposition (ASD), a technique that enables precise deposition on specific material surface, is promising for the fabrication of fully self-aligned vias (FSAV) for solving above challenges. ASD processes relying on inherent surface differences circumvents additional processing steps for surface pre-functionalization. However, these methods often suffer from a loss of selectivity after extended number of deposition cycles due to inevitable nucleation on the non-growth surface. Here, we report a novel ASD strategy for SiOC(H) thin film based on etching enhancement achieved through selective ring-opening of cyclosiloxane precursor. *In-situ* DRIFT spectra reveal ring-opening of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3) precursor on cobalt oxide surfaces. Furthermore, we demonstrate that ring-opening promotes the plasma etching rate. Based on these findings, we developed an etching-enhanced ASD which integrates molecular layer deposition and plasma etching in A-B-C supercycles. We obtained an exceptionally high area selectivity for SiOC(H) thin films on Co/SiO_2 patterns even after extended number of cycles. Cross-section TEM and high-resolution EDX mapping images confirm negligible nucleation on the CoO_x surface. Our work pioneers the exploration of precursor isomerization for etching-enhanced ASD and offers a new strategy for self-aligned SiOC(H) patterns.

3:00pm **AS-WeA-7 Area-Selective Molecular Layer Deposition of Polymer Thin Films for Contact Hole/Trench Shrinking**, ***Pengzhe Cai**, Junjie Zhao,* Zhejiang University, China

With the rapid advancement of integrated circuit technology nodes, the demand for critical size shrinking in nano-fabrication has been growing. The traditional lithography-etching method struggles to achieve the desired pitch size while maintaining cost efficiency. Contact hole/trench shrinking is a post-processing step applied before or after etching transfer, enabling patterns that exceed the lithographic resolution limit. However, when used in back-end-of-line fabrication, contact hole/trench shrinking faces the limitations of conventional wet chemistry, which restricts its full potential. Here, we report an area-selective deposition (ASD) method for contact hole/trench shrinking. We developed a plasma-enhanced initiated molecular layer deposition (PEiMLD) process that selectively grows polymer thin films onto previously defined photoresist patterns. In this all-dry PEiMLD process, remote plasma activation on the polymer backbones of the photoresist initiates radical polymerization, grafting molecular layers to the photoresist. In contrast, common dielectric surfaces (e.g. SiO_2) are inert to such activation and thus maintained as non-growth surfaces. Thereby, we achieved an area selectivity as high as 95% on PMMA/SiO_2 substrates and demonstrated contact hole/trench shrinking by reducing the trench diameter from 126 nm to 24 nm. Moreover, attributing to the versatile options of monomers for radical polymerization, this PEiMLD method can also be applied to interfacial engineering, enabling potential applications beyond contact hole/trench shrinking. Our method paves the way for alternative nanofabrication strategies that are promising for reducing the demand for lithography and lowering manufacturing costs.

3:15pm **AS-WeA-8 Catalytic Oxygen Dissociation for Area-Selective HfO_2 Deposition on Cobalt through Selective PMMA Etching**, ***Enzo Novoselic**, Christophe Vallée, Natalya Tokranova,* University at Albany-SUNY

Area-selective deposition (ASD) of thin films is critical for advanced semiconductor manufacturing, yet conventional methods often suffer from "mushrooming" defects due to poor selectivity at feature edges and lateral expansion of the isotropic growth. This work presents an alternative approach to ASD on cobalt (Co) substrates while avoiding mushrooming, leveraging catalytic dissociation for both polymer etching and selective deposition. The use of selective catalytic dissociation has been demonstrated for the etching and deposition steps. As an example, Zhang et al. [1] demonstrated selective etching on Pt/Ru/Cu/Ti, while Joseph et al. [2] demonstrated selective deposition on Pt. In this work, a polymethyl methacrylate (PMMA) material is non-selectively deposited on all exposed surfaces (Co and silicon). Through catalytic O_2 dissociation, PMMA atop Co is selectively etched in an atomic layer deposition (ALD) tool, while PMMA on silicon remains intact. Subsequently, the ALD step is performed in the same chamber at the same surface temperature, and under catalytic conditions, enabling selective growth on Co while suppressing nucleation on PMMA. Finally, PMMA is stripped, yielding structures exclusively on Co with sub-nanometer precision and vertical sidewalls.

We expect to show results demonstrating that the catalytic processes achieve near-complete selectivity and eliminate lateral overgrowth, addressing the mushrooming effect common in ASD. The use of catalytic dissociation for both etching and deposition steps simplifies integration into existing fabrication workflows. This approach offers a scalable pathway for advanced node patterning, particularly in back-end-of-line (BEOL) metallization and gate oxide applications where material selectivity and feature definition are paramount.

[1] Zhang, C.; Leskelä, M.; Ritala, M. Self-Aligned Thin-Film Patterning by Area-Selective Etching of Polymers. Coatings 2021, 11, 1124. https://doi.org/10.3390/coatings11091124

[2] Joseph A. Singh, Nick F. W. Thissen, Woo-Hee Kim, Hannah Johnson, Wilhelmus M. M. Kessels, Ageeth A. Bol, Stacey F. Bent, and Adriaan J. M. Mackus. Chemistry of Materials 2018 30 (3), 663-670. https://doi.org/10.1021/acs.chemmater.7b03818

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