

## Area Selective ALD

### Room Event Hall - Session AS-TuP

#### Area Selective ALD Poster Session

##### AS-TuP-1 Advancing AS-ALD of WSe<sub>2</sub> Through Nature-Inspired Engineering, *Kylee Lamberson, Chih-hung Chang*, Oregon State University

Area-selective atomic layer deposition (AS-ALD) of WSe<sub>2</sub> offers significant promise for advancing electronic and energy technologies. Our research introduces an innovative approach that combines microreactor-assisted nanomaterial deposition (MAND) with nature-inspired chemical engineering (NICE) to achieve safe, efficient, and lithography-free deposition with enhanced temporal resolution of nanomaterials like WSe<sub>2</sub>. Drawing inspiration from the ovipositor mechanism of the parasitic wasp *Diachasmimorpha longicaudata*, we developed a bio-inspired seed pretreatment strategy to optimize substrate surface preparation. This method utilizes a deposition nozzle to locate the seed material precisely, mimicking the wasp's ability to find a host organism for egg deposition. In our MAND system, selenium is generated in situ via a reaction between solid selenium powder and forming gas, eliminating the need for hazardous bulk storage of H<sub>2</sub>Se. Tungsten is introduced through pulsed heating of solid W(CO)<sub>6</sub>, generating tungsten carbonyl molecules. Then, alternating flows of W(CO)<sub>6</sub>, inert gas, and H<sub>2</sub>Se facilitate the selective deposition of WSe<sub>2</sub> onto micro- and nanoscale seeds. Seed shape and chemical properties were optimized using insights from literature and density functional theory (DFT) simulations. By varying source transport rates, we studied the nucleation and growth of WSe<sub>2</sub>, enabling detailed analysis of growth kinetics and process optimization. Advanced characterization techniques, including scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), were employed to validate and refine the process. This work highlights the transformative potential of integrating NICE and MAND for scalable, safe, and efficient AS-ALD of WSe<sub>2</sub>, paving the way for innovative advancements in semiconductor manufacturing and energy technologies.

##### AS-TuP-2 Advancements in Area-Selective Deposition by Merck: From Fundamental Principles to Industrial Applications, *Isiah Liu*, Merck KGaA, Darmstadt, Taiwan; *Lanxia Cheng, Tingmin Wang, Matthew MacDonald, Bhushan Zope*, Merck KGaA, Darmstadt; *Chang-won Lee*, Merck KGaA, Darmstadt, Korea (Democratic People's Republic of); *Masashi Jingui, 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 (SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, 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 Trimethylaluminum Adsorption on SiO<sub>2</sub>, 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 Trimethylaluminum (TMA) molecule on H-terminated Si, OH-terminated SiO<sub>2</sub>, and NH-, OH- and F-terminated SiN substrates (Fig1(a)). Here, TMA is a well-known precursor that is often used for Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>) 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<sub>2</sub>(-OH), SiN(-OH), SiN(-NH), Si(-H), and SiN(-F) cases. This suggested that TMA is most likely to adsorb on the SiO<sub>2</sub>(-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<sub>2</sub>, 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<sub>2</sub> substrate, which agrees with the speculation from the simulation results. For SiN substrate, we also performed H<sub>2</sub>O 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<sub>2</sub>O 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 Suzuki*, 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.<sup>1-3</sup> 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<sup>4</sup>. 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<sub>a</sub> is almost in proportion to the adsorption energy after molecule dissociation, which is denoted as E<sub>d,ads</sub>. (Fig. 1) Such empirical relationship is similar to the well-known Bell-Evans-Polanyi principle<sup>5</sup>, so we believe E<sub>d,ads</sub> can serve as a reasonable surrogate metric for E<sub>a</sub>.

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 SiO<sub>2</sub> (SiO<sub>2</sub>-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 SiO<sub>2</sub>-OH is the largest, outperforming TMSDMA, carboxylic acids, and pyridine. Alkynes could be promising inhibitors blocking Ru surface compared to SiO<sub>2</sub>-OH.

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**AS-TuP-5 Self-Assembled Inhibitor for Area-Selective Deposition on Cu Interconnects to Lower Contact Resistance**, *Yun Ki Kim*, Samsung Electronics, Republic of Korea; *Sang Chul Youn*, Samsung Electronics Co., Republic of Korea

Beyond the 5nm node, the limitations in producing nanostructures for chip production have necessitated the adoption of new materials for Cu interconnects, as the existing Ta/TaN systems have structural limitations and performance issues that hinder their effectiveness. To overcome these challenges, area-selective atomic layer deposition (ALD) techniques are employed, wherein self-assembled monolayers (SAMs) are utilized to deactivate ALD growth on pre-patterned surfaces. In this study, SAM inhibitors were used to selectively block TaN layer formation on Cu interconnects, resulting in a significant reduction in contact resistance by approximately 63%. This reduction is primarily attributed to the prevention of direct TaN deposition on Cu, with a selectivity ratio of 2.85. Furthermore, the optimal thickness for both the SAM and TaN layers was determined to be 200 °C. At last, the long-term stability in a wide range of temperature (-20–60 °C) for 18 months was investigated, and verified the suitability for mass production chips.

**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 SiO<sub>2</sub> 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 SiO<sub>2</sub> and TiN substrates, followed by VO<sub>2</sub> deposition. SiO<sub>2</sub> 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 SiO<sub>2</sub> 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 (SiO<sub>2</sub>, 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)( $\eta^5$ -C<sub>7</sub>H<sub>7</sub>O)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)], 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 SiO<sub>2</sub> 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 SiO<sub>2</sub> 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<sub>2</sub>, 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-selective atomic layer deposition (AS-ALD) is playing a crucial role. AS-ALD is a technology that can precisely deposit nanometer-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 ( $\text{MoC}_x$ ) 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 materials for AS-ALD.

In this study, we developed molybdenum carbide ( $\text{MoC}_x$ ) thermal ALD using a novel combination of Mo precursor and co-reactant, and conducted analysis of the film properties. Notably, it was observed that the film growth behavior varied depending on the substrates by analyzing Mo areal density and film thickness.  $\text{MoC}_x$  films growth was effectively suppressed on  $\text{Al}_2\text{O}_3$  substrate, whereas significant film deposition was observed on Cu substrate. Despite being a dielectric substrate, the  $\text{SiO}_2$  substrate showed similar growth behavior to Cu, suggesting these processes preferred to suppress  $\text{MoC}_x$  deposition on  $\text{Al}_2\text{O}_3$ . The  $\text{MoC}_x$  process achieved  $\sim 10.4$  nm selective deposition on Cu over  $\text{Al}_2\text{O}_3$  (94.2 % selectivity) and  $\sim 13.9$  nm on  $\text{SiO}_2$  over  $\text{Al}_2\text{O}_3$  (92.8 % selectivity). These findings demonstrate the feasibility of selective deposition on different substrates, particularly with  $\text{Al}_2\text{O}_3$  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-dielectric applications but also between dielectrics through the inherent AS-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-11 Logic Applications of Area Selective Deposition beyond 1.4nm,** Hoon Seok Seo, Kang Sub Yim, Samsung Electronics, Republic of Korea

The scaling of semiconductor devices has significantly increased transistor density, which has improved the performance of various electrical devices ranging from computers to smartphones. Through such an evolutionary miniaturization, a semiconductor manufacturing technology has required more fine deposition and patterning techniques. However, in the existing nano-fabrication processes based on lithography, it is highly challenging to form an accurate pattern alignment and limited to handle interfacial phenomena inside device. Accordingly, the semiconductor industry has intensively focused on 'area selective deposition (ASD)'. It provides a powerful technique to yield area-selective interfaces of metal/low-k material by using the self-aligned molecules as an inhibitor. In this article, we discussed the application of ASD into logic products. In particular, we introduced the evaluation results for the reverse selective barrier metal

(RSBM) and fully aligned via (FAV) that are being applicable to the backend of line (BEOL).

**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- $\eta$ )-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ( $\text{C}_{18}\text{H}_{27}\text{IrO}_3$  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.

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