Monday Afternoon, August 5, 2024

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

Selective ALD by Area-Deactivation

Moderators: Stacey Bent, Stanford University, Cathleen Crudden, Queen's University, Canada

4:00pm AS-MoA-11 Revealing New AS-ALD Chemistries with Ab Initio Approaches: From Interpretation to Prediction , Ralf Tonner-Zech, Leipzig University, Germany INVITED

Area-selectivity is currently one of the key challenges in atomic layer deposition. The selectivity observed stems from different surface reactivities of precursors and - for inhibitor-based approaches - the inhibitor molecules. Ab initio approaches like density functional theory can help to reveal the key mechanisms underlying this selectivity. They thus help to understand experimental findings in the first step (interpretation). In the second step, theory can ideally provide design principles for inhibitors and precursors from detailed analysis of several systems (prediction). I will present our progress in both areas: (i) interpretation of new AS-ALD reactivities for small molecule inhibitor-(SMI-)based approaches to ALD on dielectric and metallic surfaces,[1] and (ii) understanding of design principles for SMIs and precursors using ab initio computations and electronic structure analysis.

 J. Yarbrough, F. Pieck, A. B. Shearer, P. Maue, R. Tonner-Zech, S. F. Bent, Chem. Mater.2023, 35, 5963–5974; (b) J. Yarbrough, F. Pieck, D. Grigjanis, I.-K. Oh, P. Maue, R. Tonner-Zech, S. F. Bent, Chem. Mater.2022, 34, 4646– 4659; (c) S. Zoha, F. Pieck, B. Gu, R. Tonner-Zech, H.-B.-R. Lee, in revision.

Funding fromaMerckKGaA, Darmstadt,Germany350thAnniversaryResearchAwardisgratefullyacknowledged.

4:30pm AS-MoA-13 Area Selective Atomic Layer Deposition Using a Size Cutter, Han-Bo-Ram (Boram) Lee, Incheon National University, Republic of Korea INVITED

Area-selective atomic layer deposition (AS-ALD) has received great attentions due to its potentials for a key toolbox in the nanofabrication of Si devices. The approach using inhibitor molecules which locally change surface chemical properties to inert toward the following ALD reactions has been widely used. The defect density of inhibitor layer which is a potential nucleation site should be minimized to achieve high selectivity, however, it is difficult due to the steric hindrance of inhibitor molecule during comparative adsorption. In this presentation, a simple approach to minimize the steric hindrance effects of inhibitor and maximize the blocking property is introduced. The ligand size of inhibitor layer could be reduced by only additional pulse of H₂O and the adsorption coverage of inhibitor could be increased. The concept of size cutter has been interpreted by using theoretical calculations with density functional theory (DFT) and Monte Carlo (MC) simulation and the results show highly consistency with experimental observation. The results could provide insights for the next generation nanofabrication in the semiconductor technology using AS-ALD.

5:00pm AS-MoA-15 Ald Grown Self-Assembled Monolayers: Using Area-Selective Deposition to Characterize Molecular Scale Pinholes, Sakari Lepikko, R. Ras, Aalto University, Finland

Area selective atomic layer deposition has become a key method for creating patterned thin film structures for various applications in the semiconductor industry. Self-assembled monolayers (SAMs) are often used for de-activating surfaces, to block the ALD film growth (Figure 1). SAMs allow easy patterning, are capable of inhibiting wide variety of precursors, and are suitable on various substrates. Whereas certain SAM chemistries, such as alkyl trichlorosilanes are good for de-activating oxide substrates, they are also notoriously difficult to grow defect free, thereby reducing the SAM effectiveness to block ALD growth.

A promising option is to grow the SAMs directly in the ALD reactor, as it provides dry vacuum environment with good temperature control, thus making it an ideal tool for optimizing the SAM growth. Here, we present how the quality of non-fluorinated octyltrichlorosilane SAMs can be tuned to better block growth of various ALD films with differently sized precursor molecules [1]. By increasing SAM growth time its areal coverage increases, which leads to reduction of pinholes in the SAM and thus to the adsorption sites for the ALD reactant molecules (Figure 2). We also show that the maximal pinhole size reduces with the increasing coverage, which helps blocking adsorption of smaller ALD precursor molecules such as diethyl zinc. We see that growing SAMs directly in an ALD reactor could provide means to create more uniform SAMs with better resistivity against various ALD precursors, thus helping fabrication of even more demanding nanostructures in the semiconductor field.

We demonstrate that these SAMs have tunable hydrophobicity with extraordinarily low droplet friction. We demonstrate the world's most slippery surface by coating of SAM on black silicon.[1]

Lepikko, S., *et al.* Droplet slipperiness despite surface heterogeneity at molecular scale. *Nature Chemistry* (2024). https://doi.org/10.1038/s41557-023-01346-3

5:15pm AS-MoA-16 Area-Selective Etching of Poly(lactic acid) via Hydrogenolysis for Self-Aligned ALD, Valtteri Lasonen, M. Ritala, University of Helsinki, Finland

Our previous works have demonstrated that area-selective etching (ASE) of polymers is a novel approach for enabling self-aligned ALD.^{1,2} In ASE, a polymer film is decomposed only on catalytic surfaces whereas on noncatalytic surfaces the polymer stays intact. ASE was demonstrated in the air using Pt as the catalytic and native SiO₂ as the non-catalytic surface with two polymers, polyimide and poly(methyl methacrylate) (PMMA). After the ASE of polyimide, ALD-Ir grew only on the exposed Pt surface, whereas no growth was observed on the polyimide. In the case of ASE of PMMA, small amount of ALD-Ni growth occurred also on PMMA. However, a simple liftoff after the ALD removed the unwanted Ni. Other catalytic surfaces were also identified, such as CeO2 . Furthermore, it was demonstrated that only a small amount of ALD-Pt or ALD-CeO2, even down to a fraction of a monolayer, was enough to show a clear catalytic effect. This means that small amounts of Pt can be deposited on a metal surface, and CeO2 on an insulator surface, to catalytically activate them. This is important because neither Pt nor CeO₂ is commonly used in semiconductor devices.

Many materials used in semiconductor devices are prone to oxidation when heated in the air, thus, non-oxidative atmospheres must be found for ASE. Two such atmospheres, inert (99.999% N₂) and H₂ (5% H₂ in Ar), were tested with PMMA and polyimide.^{1,2} Out of all the surfaces tested only Ti, Pd, and Cu showed some catalytic effect in the inert atmosphere and/or in the presence of H₂. For example, the well-known hydrogenolysis catalyst, Pt, did not show any catalytic effect on the decomposition of PMMA in the presence of H₂. This is most likely because PMMA is not susceptible to hydrogenolysis, unlike condensation polymers, such as poly(lactic acid) (PLA). Here, we demonstrate that PLA is catalytically decomposed on several known hydrogenolysis catalysts, such as Pt, Ir, and Ni in the presence of H₂ whereas in the inert atmosphere PLA films stay intact on these surfaces at the same temperatures. Additionally, Co is demonstrated to work as a catalytic surface also in the inert atmosphere. In this case the removal mechanism is catalytic cracking of the polymer. These new findings give us confidence that ASE of polymers is possible with plethora of different surface combinations by carefully choosing the right catalytic material, polymer, and atmosphere, thus allowing new self-aligned ALD processes.

References

1. Zhang et al. Coatings. 2021, 11(9), 1124.

2. Lasonen et al. Chem. Mater. 2023,35(15), 6097-6108.

5:30pm AS-MoA-17 Selective Surface Fluorination to Enable ASD of Polymer and Metal Oxide on SiN vs. SiO₂, Jeremy Thelven, H. Oh, H. Margavio, C. Oldham, G. Parsons, North Carolina State University

3D integration of semiconductor devices such as Gate-All-Around FETs and vertical device stacking is being implemented to reduce power consumption and enable further scaling for logic and memory devices.¹ There is a critical need to reduce the processing budgets to achieve such advanced designs and area-selective deposition (ASD) offers a bottom-up approach to achieve the desired scaling goals.² The ability to selectively react and deposit on an oxide vs nitride surface is widely recognized as key roadblock for scaling due to the chemical similarity of these surfaces. ASD on nitride vs oxide surfaces, or vice versa will provide new options for patterning, to improve self-alignment, and to reduce edge placement errors. In this work, we demonstrate the use of a selective surface fluorination treatment to promote ASD on SiN vs. SiO₂.

To demonstrate ASD on SiN vs. SiO₂, we explored a surface treatment using molybdenum hexafluoride (MoF₆) on blanket SiN and SiO₂ wafers. Next, we deposited about 50nm of polypyrole (PPy) CVD on both surfaces. We found that PPy proceeded to grow as a film on the SiN surface after a brief nucleation delay, while only showing isolated nuclei on the fluorinated SiO₂ surface. As a further demonstration, experiments were performed on

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patterned SiO₂/SiN wafers which further confirmed PPy selective growth. We believe the MoF₆ exposure leads to the fluorination of both surfaces, which was confirmed by XPS, where this fluorination selectively passivates PPy growth on the SiO₂ surface. To extend this demonstration of ASD on SiN vs SiO₂ to other types of materials, we recently tested the treatment with the deposition of TiO₂ through ALD. We found that this selective fluorination passivation of the SiO₂ surface allows for selective growth of TiO₂ on SiN. The mechanisms behind selectivity, and the extent of passivation are currently under investigation by our group.

1 Datta, S.; Dutta, S.; Grisafe, B.; Smith, J.; Srinivasa, S.; Ye, H. Back-End-of-Line Compatible Transistors for Monolithic 3-D Integration. IEEE Micro 2019, 39 (6), 8–15. https://doi.org/10.1109/MM.2019.2942978.

2 Decadal Plan for Semiconductors. Semiconductor Research Corporation. https://www.src.org/about/decadal-plan/

Tuesday Morning, August 6, 2024

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

Selective ALD

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

10:45am AS-TuM-12 Novel Carbon-based Ligands on Planar Metal Surfaces: Self Assembled Monolayers and Applications in Atomic Layer Deposition, Cathleen Crudden, Queen's University, Canada INVITED The use of N-heterocyclic carbenes to modify homogeneous metal catalysts is widespread since the high metal–carbon bond strength renders high oxidative and chemical stability to the resulting metal complexes. The use of these carbon-based ligands to modify metal surfaces has received considerably less attention. We will describe the modification of planar metallic surfaces with carbene ligands. The nature of the surface overlayer is strongly dependent on the structure of the carbene. The ability of these carbene overlayers to bind to a range of metals and act as small molecule inhibitors for atomic layer deposition processes will be described.

11:15am AS-TuM-14 Enhancing Selectivity for AS-ALD of MoO₂ through Hydrogen Treatment: Strategy of Surface Cleaning and Expanding Deactivated Areas, *Hae Lin Yang*, *J. Kwon*, *C. Park*, Hanyang University, Korea; *S. Lee*, *B. Kim*, *C. Jung*, *H. Lim*, Samsung Electronics Co., Inc., Republic of Korea; *J. Park*, Hanyang University, Korea

Recently, in the field of DRAM capacitors, the demands for precisely depositing MoO₂ thin films for resolving the high leakage issue between high-k dielectric and TiN electrodes, onto TiN without additional patterning¹. To meet these demands, Area selective atomic layer deposition (AS-ALD), which allows selective deposition on certain areas without undesired deposition on adjacent areas, is essential. Also accomplish the high selectivity of high-resolution films with high spatial resolution, the introduction of inhibitors is needed especially small molecular inhibitors (SMIs). SMIs consist of inert tail portions composed of single molecules, enabling them to have small sizes suitable for narrow lines at the nanometer scale. However, SMIs typically have short tail groups that cannot undergo van der Waals interactions, and they cannot densely cover the substrate surface due to steric hindrance from adjacent adsorbed SMIs during precursor adsorption². Therefore, considerations regarding the treatment of unadsorbed areas and the removal of remaining reactive groups after SMI adsorption are necessary. To address this, we added a hydrogen treatment process during the AS-ALD process of MoO₂ using TCPS [C₆H₅SiCl₃] and DMA-TMS [(CH₃)₃SiN(CH₃)₂] as SMIs and analyzed the effects of hydrogen treatment on surface properties and selectivity using XPS, WCA, and AES mapping. Additionally, we calculated reaction energies for each adsorption step and final forms for each SMI-adhered surface using DFT and RSA simulations. TCPS, owing to its aromatic phenyl ring, covers a wider range of SiO₂ surfaces than DMA-TMS. However, only two out of three Cl ligands react, leaving about 1.4% of the remaining Cl ligands after TCPS adsorption, increasing the surface energy and acting as adsorption sites for Mo precursors. However, by adding a hydrogen treatment cycle during the process, all remaining Cl ligands were removed, resulting in a 13° increase in WCA and a dramatic increase in selectivity from 61% to 96%. Furthermore, hydrogen treatment not only removed residual impurities but also reduced exposed -OH groups on the surface by converting them to -H, as confirmed by the results of hydrogen treatment added during the DMA-TMS process. Despite the absence of impurities to be removed, the WCA increased by approximately 7° after hydrogen treatment, and the selectivity also increased from 84% to 94.5%. In this way, appropriate treatments during AS-ALD processes, though simple, can effectively increase selectivity, enabling precise selective deposition in desired areas even in complex structures.

11:30am AS-TuM-15 Contra-Selective Deposition of SiO₂ on Metals, Chad Brick, T. Ogata, Gelest, Inc

In recent years, an increasing number of area selective processes have been developed for the deposition of dielectric films on dielectric layers. However, reports of the selective deposition of dielectric films on metal regions of a substrate are comparatively rare, typically involving the deposition of high-k dielectric films with significantly different chemistry with respect to the target low-k non-growth areas such as SiO₂ or SiN. In this study, a series of heteroatom-containing silanes with inherent selectivity towards metals over SiO2 and SiN and their conversion to SiO2 via plasma-enhanced atomic layer deposition have been investigated. It will

be shown that under appropriate conditions, indefinitely thick films of SiO2 can be selectively grown on metals such as copper and cobalt with preexisting native or thermal silicon dioxide as the non-growth substrate. Mechanisms of this unusual "contra-selectivity", with a film growing not only on a material other than itself with its unblocked self as a non-growth surface, but also continuing to grow to arbitrary thickness despite the nearidentical nature of the growth and non-growth surfaces after the first few deposition cycles, will be discussed.

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

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

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

References:

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

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

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

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

Area Selective ALD Room Hall 3 - Session AS-TuP

Area Selective ALD Poster Session

AS-TuP-1 Selective Metal Blocking using Vapor-Phase Self-Assembled Monolayers for Area-Selective Atomic Layer Deposition of Dielectrics, Jeong-Min Lee, W. Kim, Hanyang University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) offers complementary bottom-up patterning with atomic-level accuracy on pre-defined areas in conjunction with conventional top-down patterning, so it has attracted tremendous interest for enablement of multi-dimensional nanostructures toward sub-10 nm scale technology. In this study, we report a methodology for achieving selective deposition of dielectric thin films by using vaporphase self-assembled monolayers (SAMs) accompanied by post-surface treatment. First, we investigated the AS-ALD of ZrO2 films for dielectric versus metal selectivity through vapor-phase phosphonic acid (PA) SAMs treatment with long alkyl chains. The blocking capability of PA SAMs was comparatively evaluated with O_3 and O_2 reactants on SiO₂, TiN, and W substrates, and we confirmed that a relatively high deposition selectivity above 0.9 can be achieved even after ALD 200 cycles with mild oxidizing reactant. Further, electrical properties of ZrO₂ films deposited with both reactants were also investigated comparatively with and without postsurface treatment, and as a result, it was demonstrated that high-quality ZrO_2 films with high dielectric constant can be fabricated through the postsurface treatment. Second, we confirmed the AS-ALD of SiO₂ films only on SiO₂ substrates through vapor-phase functionalization of PA SAMs with fluoroalkyl chains. By using the mild oxidant in subsequent ALD process, selective deposition of SiO₂ thin films over ~8 nm on SiO₂ versus TiN and W substrates was successfully demonstrated.We anticipate that this work provides a new strategy to achieve highly selective deposition for AS-ALD of dielectric on dielectric (DoD) application toward the upcoming bottom-up 3D nanofabrication.

AS-TuP-2 Area-Selective ALD of Transparent Conductive Oxides by Using Polymer Patterns Generated with High-Precision Capillary Printing, *Ludovic Hahn*, CEA-LETI, France; *M. Pascual, A. Guitton, K. Farmand, A. M'Barki*, Hummink, France; *T. Jullien, L. Golanski, C. Guerin, V. Jousseaume*, CEA-LETI, France

Transparent conductive oxide thin films are widely developed for numerous applications in optoelectronics due to their unique properties. However, the oxide film needs to undergo patterning, which is often difficult to achieve with standard lithographic steps. Indeed, those materials are difficult to integrate due to their sensitivity to chemistry, like ZnO, which is water-sensitive. This problem becomes even more dominant when reducing the features for further application. An alternative to photolithographic steps is Area Selective Deposition (ASD), which uses an inhibiting layer such as a polymeric film that prevents oxide deposition on certain controlled regions.

In this work, polymeric films were printed by an innovative direct nanoprinting technique [1]. This High Precision Capillary Printing (HPCAP) technique is based on AFM technologies. A nanopipette filled with the ink of interest will oscillate at a high frequency and deposit the ink to form complex geometries at the surface of a substrate. A precision of 20 nm in the xy plane and a resolution between 100 nm and tens of microns can be achieved, which, coupled with a high deposition rate, makes it a good alternative for additive manufacturing.

Micrometric patterns of polymers, comprising poly(methyl methacrylate) (PMMA), poly(vinyl pyrrolidone) (PVP) and an epoxy-based resist (SU-8) were drawn on silicon substrate. Then TCO, such as ZnO and SnO2, were deposited on the patterned polymers by low-temperature ALD. By using spectroscopic ellipsometry, atomic force microscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy, it is shown that PMMA inhibits both oxides, compared to PVP and SU-8, which only suppress ZnO growth. Moreover, an exclusion zone around the polymer pattern where oxides are inhibited is observed, depending on the polymer used. The study of the impact of the pattern size (from a few μ m to a few tens of μ m) reveals that this exclusion zone is independent of the geometry but mainly depends on the polymer used and the type of oxide deposited.

Finally, the polymers can be selectively removed leading to a selective deposition of TCO and a 10 μm pixel array was successfully produced. This original approach combining the direct nanoprinting of a polymer pattern

with the subsequent ALD deposition of TCO appears to be a promising path for the patterning of a sub-10 μ m matrix of pixels.

[1] M. Pascual, N. Bigan, A. M'Barki, R. Mental, I. Allegro, U. Lemmer, SPIE Opto 2023, 124330E

AS-TuP-3 Photo-Enhanced Selective Area Atomic Layer Deposition, Paul Butler, Walter Schottky Institut, Technische Universität München, Germany; L. Sortino, Ludwig-Maximilians-University of Munich, Germany; S. Maier, Monash University, Australia; I. Sharp, Walter Schottky Institut, Technische Universität München, Germany

One of the major challenges that ALD currently faces is the lack of lateral control, which has led to an ongoing interest in selective-area ALD (SA-ALD) techniques that can allow for bottom-up fabrication of micro- and nanostructures. In this respect, photo-enhanced ALD (photo-ALD), in which welldefined photoexcitation is used to activate chemical reactions at certain areas on a surface, holds significant promise for SA-ALD. However, relatively few studies on photo-ALD have been conducted and the spatial resolution of this technique remains limited. Here, we present a novel approach to achieving SA-ALD via in situ photoexcitation of the surface. Our experiments demonstrate that optical laser excitation enhances ALDgrowth of TiO₂ films on gold substrates, with the deposition rate increasing with laser intensity. To investigate the photo-induced reaction, gold-coated silicon substrates were sequentially exposed to titanium isopropoxide (TTIP) and ozone outside the normal ALD process window, with some substrates exposed to illumination from a 515 nm laser. Using in situ spectroscopic ellipsometry to monitor the growth rate of the TiO₂ films during the ALD deposition, we find an illumination-activated growth that can be assigned to enhanced oxidation of the adsorbed precursor. Furthermore, patterned illumination through a shadow mask results in laterally structured growth, as verified by ex situ ellipsometry mapping. Ongoing work is now devoted to identifying thermal and electronic contributions to the growth mechanism, as well as coupling the exciting illumination to plasmonic gold nanostructures. Overall, this method of selective-area photo-ALD could later be applicable to bottom-up nanofabrication, with applications ranging from nanoscale optoelectronics to photocatalysis.

AS-TuP-4 Area-Selective Atomic Layer Deposition of Bilayer Materials Using Polymethylmethacrylate Thin Films as Blocking Layers, Aditya Chalishazar, N. Poonkottil, C. Detavernier, J. Dendooven, Ghent University, Belgium

Area-selective ALD (AS-ALD) is an interesting subset of ALD where materials are selectively grown on specific areas of the substrate. As an additive bottom-up approach, it has immense potential for reducing the number of steps in nanomanufacturing [1-3].

AS-ALD studies have mostly been limited to single-material deposition. Multi-material AS-ALD poses additional challenges as it requires the ALD process chemistries to be compatible in their temperature windows and chemical selectivity. Realizing multi-material ASD has become an interesting challenge in recent years [2,4]. In particular, selective deposition of multilayers can substantially reduce processing time for the fabrication of nanoscale devices.

In this work, we explore the use of metal dialkylamide precursors with polymethylmethacrylate (PMMA) masking layers to realise multi-material AS-ALD. PMMA is a popular AS-ALD inhibitor layer: it can be patterned using various approaches and can easily be removed using exposure to plasma or dissolution in appropriate solvents [3,5].

Here, ALD of SnO₂ and Ta₂O₅ using their dialkylamide precursors and water at 120 °C was performed on Si and blanket PMMA substrates. Selective deposition of SnO₂ and Ta₂O₅ is obtained on Si with negligible deposition on the PMMA blanket substrate after 100 cycles (Figure 1), which was confirmed by XRR/XRF and XPS measurements. SnO2 was then deposited on a PMMA patterned wafer and studied using energy dispersive X-ray spectroscopy (EDS), which showed deposition between the PMMA pattern (Figure 2a-c). The films were imaged after plasma treatment, which resulted in a SnO2 pattern (Figure 2d-f). Extending this concept, we deposited a SnO₂-Ta₂O₅ bilayer using a PMMA masking pattern, followed by mask removal with oxygen plasma (Figure 3). This demonstrates the deposition of a multilayer material using one template material without the need for intermediate processing steps. We believe such a combinatorial approach using metal dialkylamide precursors and PMMA can open new avenues to the deposition of patterned multilayer devices for device manufacturing using AS-ALD.

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[1]Chemistry		of	N	Materials,2018,		31,	2-12					
[2]	Chemistry	of	Mat	erials,	2023,	35,	4375-4384					
[3]	Advanced	Mate	erials	Interj	faces,2023,	10,	2201934					
[4] ACS	Na	Nano,)21 ,	15,	12276-1228						
[5] Chemistry of Materials, 2020, 32, 4920-4953												

AS-TuP-5 Density Functional Theory Study on Selective Silylation of SiO₂ Against Cu Using Dimethylaminotrimethylsilane, *Misoo Kim*, *K. Khumaini*, *R. Hidayat*, *H. Kim*, *W. Lee*, Sejong University, Republic of Korea

Selective cobalt capping of the copper surface has been introduced to improve the electromigration resistance of copper interconnects. Chemical vapor deposition of cobalt on copper is inherently selective against silicon oxide, and the selectivity can be enhanced by silylation of the oxide surface to form an alkyl-terminated surface. In the previous work, we studied the selective chemisorption of the cobalt precursor on copper and showed that chemisorption is favored on copper but not on silicon oxide. We also showed that physisorption and chemisorption of the cobalt precursor are more difficult on alkyl-terminated SiO₂ than on OH-terminated SiO₂ [1]. Recently, another research group demonstrated that the alkyl-terminated surface is also essential for the selective atomic layer deposition of films They observed ruthenium [2]. that at 250°C dimethylaminotrimethylsilane (DMATMS) readily reacts with surface -OH groups on SiO₂ to form –O–Si(CH₃)₃ groups. However, the theoretical study of the reaction mechanism to form an alkyl-terminated silicon dioxide surface is rare. In addition, the reaction of DMATMS with metallic surfaces has not been reported by either experimental or theoretical studies. In the present work, we performed density functional theory (DFT) calculations to study the reaction mechanism for the selective silvlation of DMATMS on silicon oxide against copper surfaces. We constructed two substrates, vicinal OH-terminated SiO₂ and bare copper substrate. All possible chemisorption pathways were considered. The reaction and activation energies of chemisorption on these two surfaces were calculated and compared. In addition, the Gibbs free energy changes for silylation were determined to explain the selective silulation at process temperature. The results can provide fundamental insights into the selective surface inhibition mechanism for area-selective deposition.

Acknowledgments

References

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AS-TuP-6 Self-Aligned Patterning of Tantalum Oxide on Cu/SiO₂ with Inherent Selective Atomic Layer Deposition, *Kun Cao*, *Z*. *Qi*, State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China; *B. Shan*, State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China; *R. Chen*, State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

The chemical principal and mechanisms that enable selective atomic layer depositions are gaining rapid growing interests, which have unlocked attractive avenues for the development of novel nanostructures by depositing atoms at desired surface locations. In this talk, the inherently selective atomic layer deposition processes will be discussed. Tantalum oxide was studied on a series of oxide substrates. Although the oxides have -OH groups on the surface and proposed to have similar nucleation sites, there are long nucleation delays on basic oxides. The H-transfer reaction is a key factor to influence the reaction barrier. It is hard to nucleate on basic substrates because the H-transfer reaction is blocked. Another demonstration is the redox-coupled inherently selective ALD for selfalignment of tantalum oxide on SiO₂/Cu nanopatterns. By adding an in-situ ethanol reduction pulse before each traditional binary ALD cycle, and the 'reduction-adsorption-oxidation' ALD process increases the selectivity. Selfaligned manufacturing on nanoscale Cu/SiO2 patterns without excessive mushroom growth at the edge and undesired nucleation defects on the Cu region. The process can be reliably repeated to yield more than 5 nm-thick Ta₂O₅ on the SiO₂ region, while no undesired deposition occurs on Cu patterns. In addition, an anisotropic growth model with the dynamical competition of expansion and dissociation of the nucleus is proposed to nucleation delay are quantitively predicted and the model provides a practical method to evaluate the selectivity of ALD theoretically.

AS-TuP-7 Bottom-up Plasma-Enhanced Atomic Layer Deposition of SiO₂ in High Aspect Ratio Trenches using NF₃ Inhibitor, Martial Santorelli, Université Grenoble Alpes, CNRS, LTM, STMicroelectronics,, France; J. Tortai, Université Grenoble Alpes, CNRS, LTM, France; M. Querré, STMicroelectronics, France; M. Bonvalot, Université Grenoble Alpes, CNRS, LTM, J-FAST, Institute of Applied Physics, Faculty of Pure and Applied Sciences, University of Tsukuba, Japan

With the continuous size reduction of pixels of CMOS optical sensors, one of the main innovations consists in implementing optical pixels in the back-face of the chip, so that the high flux of light does not have to cross the metal wiring region (Fig. 1). This, in turn, provides increased light absorption and enhanced sensitivity, thereby allowing pixels downscaling, leading to high-resolution image sensors. However, this solution brings new technical challenges, which must be addressed, such as parasitic charge transfer between neighboring pixels are separated by Deep Trench Isolators (DTI), which are most commonly filled with SiO₂. At each new generation of optical sensor, the DTI aspect ratio (AR) is gradually increasing [1]. Thus, the correct trench filling of such high AR structures by SiO₂ becomes a true technical challenge (Fig. 2a).

Plasma Enhanced Atomic Layer Deposition (PEALD) is the most appropriate deposition process for this purpose, due to its high degree of conformality, although it leads to seam or void formation in the depth of high AR trenches. Such defects are thought to originate from the formation of an overhang of precursor adsorbates at the trench opening, due to the higher concentration of reactants, which leads to a higher surface growth rate (Fig. 2b).

In this work, we have investigated the possibility of inserting an additional inhibiting NF₃ plasma step within the PEALD cycle. It focuses on the involved inhibition mechanisms and highlights the dependence of the filling depth on the trench opening dimension and plasma process parameters. Inhibition mechanisms are analyzed by ellipsometry and XPS and diffusion depth by SEM, coupled with FIBSEM/TEM. The optimization of the periodicity of the NF₃ plasma step leading to the best trench filling is discussed in detail. This study should facilitate future process developments addressing trench filling with critical width and depth dimensions.

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AS-TuP-8 What Happens to Small Molecule Inhibitors after the Selectivity Is Lost: 4-Fluorophenylboronic Acid Functionalization of Silicon Surface to Inhibit TiO₂ Deposition, Andrew Teplyakov, D. Silva-Quinones, J. Mason, R. Norden, University of Delaware

As the size of the components in electronic devices decreases, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing. Organic monolayers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods. However, choosing the appropriate surface modification requires knowledge of the corresponding chemistry and also a detailed investigation of the behavior of the functionalized surface in realistic deposition schemes. The 4fluorophenylboronic acid (FPBA) can be used as a model to investigate the possibility to utilize the Si(100) surface functionalized with this compound as a non-growth substrate in a titanium dioxide (TiO_2) deposition scheme based on sequential doses of tetrakis(dimethylamido)titanium (TDMAT) and water and to follow what happens at the interface when the selectivity is eventually lost. A combination of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) allows for a better understanding of the process. The functionalized surface is shown to be as effective non-growth area to TiO₂ deposition when compared to currently used H-terminated silicon surfaces but to exhibit much higher stability in ambient conditions. Thermal treatment and analysis of F and B labels allow for investigating interface stability and opportunities to use the scheme for monolayer doping.

AS-TuP-9 Modelling the Reactivity of Small Molecule Inhibitors by Density Functional Theory, Fabian Pieck, R. Tonner-Zech, Wilhelm-Ostwald Institut for Physical and Theoretical Chemistry, Leipzig University, Germany

Within area-selective atomic layer deposition selectivity is achieved by various approaches. We follow the strategy to block growth on the nongrowth surface by the deposition of small molecule inhibitors (SMIs) prior to the atomic layer deposition (ALD) process. Here, the selectivity of the process can be improved by understanding the properties and reactivity of the SMIs at an atomic level. Especially, tuning the SMIs with respect to the studied surface and ALD process based on their blocking mechanism is

highly valuable. To understand the impact of the SMI structure on its reactivity we are studying two classes of SMIs namely sulfur-based SMIs as diethyl sulfide¹, dipropyl sulfide and diisopropyl sulfide as well as nitrogenbased SMIs as aniline, pyridine and pyrrole (Figure 1). With SiO₂, Cu(111) and CuO(111) common metal and oxide surfaces are considered as substrate while these classes of SMIs are experimentally investigated for the deposition of HfO₂ and Al₂O₃, respectively.

We use ab initio modelling by density functional theory (DFT) to explore adsorption properties and on-surface reactivity of SMIs. Here, adsorption energies are used to find the most stable adsorption structures, while changes in the adsorption energies for multiple adsorbates help to identify ideal inter-molecular spacing and SMI packing density. Reaction paths and transition states are obtained by the nudged elastic band method while obtained activation energies reveal the most likely reactions. In addition, kinetic Monte Carlo (kMC) simulations are used to clarify the impact of obtained intermediates and side reactions on the desired product formation.

1. S. Zoha, F. Pieck, B. Gu, R. Tonner-Zech, H.-B.-R. Lee, Organosulfide Inhibitor Instigated Passivation of Multiple Substrates for Area-Selective Atomic Layer Deposition of HfO₂. *Chem. Mater.* 2024 accepted.

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

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

We have synthesized a family of novel polyfluorinated isonitriles with different chain lengths for use as a SMI in AS-ALD. As an example, Long Chain Inhibitor is readily synthesized in two steps from the amine and is volatile, with a 1 Torr vapour pressure at 33 °C. This compund shows promising selectivity for adsorption to metals over oxides as measured via quartz crystal microbalance (QCM), saturating gold with a surface density of 62 ng/cm² (0.81 molecules/nm²) with concurrently negligible adsorption on alumina (Figure 1). The synthesis and thermal characterization of several fluorinated isonitriles will be discussed. Their selectivity for metal surfaces by QCM, as well as ToF-SIMS mapping on metal/SiO₂ patterned substrates will be shown to demonstrate selectivity, with excellent resolution provided by the high fluorine content of the molecule. Selective inhibition of zinc oxide ALD will also be discussed and selectivity values will be reported.

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AS-TuP-11 Atomic Layer Plasma Treatment for Area-Selective Atomic Layer Deposition of High-Quality SiO₂ Thin Film, Sanghun Lee, S. Seo, T. Kim, H. Yoon, S. Park, S. Na, J. Seo, Yonsei University, Republic of Korea; W. Noh, Air Liquide, Republic of Korea; S. Chung, H. Kim, Yonsei University, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) has been intensively studied due to its demonstrated versatility in recent nanotechnology applications. The priority focus in AS-ALD is achieving the desired selectivity; thus, most studies to date have concentrated on the reaction mechanism of ALD on the growth/non-growth substrate or sought novel methodologies to resolve challenges in its implementation in high-volume manufacturing. On the other hand, the qualities of film deposited by AS-ALD were usually not highlighted. In this work, we studied the AS-ALD approaches that could enhance the selectivity and film quality simultaneously. We developed AS-ALD SiO₂ on SiO₂ whereas SiO₂ was not grown on SiN_x. NH₃ plasma pre-treatment was employed to functionalize SiN_x surface with more –NH species which are known for their lower

reactivity toward Si precursors. The results show that NH₃ plasma pretreatment is effective in increasing selectivity, but the plasma condition needs to be controlled to avoid inducing damage to the SiN_x surface, which could offer reactive sites for precursor adsorption. We carried out ALD supercycle of NH₃ plasma pre-treatment and ALD SiO₂ to achieve higher selectivity. When the number of NH₃ pre-plasma treatment cycles was increased, the growth of SiO₂ on SiN_x was further delayed. Furthermore, layer-by-layer NH₃ plasma pre-treatment densified the SiO₂ film owing to ion bombardment, as revealed in etching characteristics and x-ray reflection spectra. Moreover, NH₃ plasma pre-treatment did not result in incorporation of nitrogen into growing SiO₂ film as analyzed by x-ray photoelectron spectroscopy. Consequently, atomic layer NH₃ plasma pretreatment enabled a higher selectivity and improved SiO₂ film quality, as evaluated by the electrical property measurement of metal-oxidesemiconductor capacitor.

AS-TuP-12 The Formation of a Bottomless ZnO Barrier Using Inherent ZnO AS-ALD Process for Advanced Metallization, Yuki Mori, TANAKA Precious Metals, Japan; Y. Son, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea; S. Kim, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea; S. Kim, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Area selective atomic layer deposition (AS-ALD) is one of the most promising technologies for next-generation interconnect. The bottomless barrier using AS-ALD can reduce interconnect resistance by the deposition of barrier material only on the via sidewall (such as SiO2/low-k) not on the via bottom (such as metal). Generally, in the previous studies, barrier materials are selectively deposited using long-chain inhibitors. Therefore, it is difficult to apply it to fine structures. Inhibitor-free inherent AS-ALD is a promising process to solve this problem. ZnO has been reported as the bottomless barrier of Cu interconnects by AS-ALD using an alkanethiol inhibitor [1]. There are many reports regarding AS-ALD of ZnO using inhibitors but the investigation on inherent inhibitor-free AS-ALD of ZnO is very limited [2] thought inhibitor-free ALD has clear advantages with device scaling-down. In this report, systematic studies on the inherent ZnO AS-ALD with substrate materials and process of substrate materials are described. Here, ALD of ZnO was basically conducted at 120 °C by using diethylzinc (DEZ) and H₂O as a precursor and a reactant, respectively. DEZ and H₂O pulsing time were 1 second, where it guarantees the self-limited growth of ZnO. The results shows that there is no incubation cycle on SiO_2 , but ~80 incubation cycle on H-terminated (Si-H). It indicates that the surface OHgroups on SiO₂ promote the adsorption of the Zn precursor, and the surface H-groups on Si-H prevent the adsorption of the Zn precursor. We also investigated about ZnO ALD on different metal surfaces and found that ALD-ZnO process shows a nucleation delay on clean metal surfaces with fewer surface OH-groups. On the easily oxidized metals (such as Ti and Cu), ALD-ZnO process shows almost no incubation cycle. The present findings are expected to enable the formation of bottomless ZnO barrier without providing any inhibitor and reduce interconnect resistance in semiconductor devices.

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AS-TuP-13 Area-Selective Atomic Layer Deposition by Sputter Yield Amplification on Heavy Elements, Arthur de Jong, M. Bär, M. Merkx, E. Kessels, A. Mackus, Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) is an emerging approach for device fabrication, that can circumvent the need for lithography for specific layers in a device stack. The selectivity between the growth and the non-growth area is typically achieved on the basis of a chemical difference, by e.g. selective precursor or inhibitor adsorption [1]. To expand the ASD toolbox, a physical approach combining a non-selective ALD process with areaselective sputter etching by ions is investigated in this work. The advantage of sputter etching is its relative independence on temperature and ALD chemistry. To enable selective etching based on sputter yield amplification, the non-growth area requires an element with a much larger mass than the incoming ion [2]. The ions generated by a plasma arrive at the surface with an inwards facing momentum. If an ion collides with an atom having a much larger mass, this momentum is redirected upwards more efficiently as compared to a collision with a light atom. This efficient redirection increases the amount of energy that is transferred to surface atoms, resulting in a larger probability to etch them. The growth area should not contain heavy elements, leading to a much smaller etch rate.

To investigate the selective sputter etching, a thin SiO_2 overlayer deposited by ALD was exposed to low-energy Ar ions. The amount of SiO_2 removed

depends significantly on the substrate material underneath (Al₂O₃, TiO₂, Nb₂O₅, MoO₃, HfO₂, Ta₂O₅ and WO₃ are investigated here). In general, the heavier the mass of the metal atoms in the substrate, the less SiO₂ is observed after the ion exposure. As demonstration for the feasibility of the approach, SiO₂ was selectively deposited on Al₂O₃ with respect to a HfO₂ non-growth area. The ASD process consists of repeating supercycles of three SiO₂ ALD cycles and Ar ion exposures from a plasma. Approximately 1.2 nm of selective growth is achieved on the Al₂O₃, while most deposition is effectively removed from the HfO₂ (<0.3 nm is observed). It is challenging to maintain the etch selectivity for thicker SiO₂ which can be mitigated by tuning the ALD process. This proof-of-concept shows that exploiting sputter yield amplification can enable ASD processes that are complementary to the existing chemical approaches.

[1]Mackus	et	al.	(2019)	Chemistry	of	Materials	31,	2
[_]	~~		(2020)	enemou y	•••	inaccinato	,	_

[2]Berg *et al.* (1992) Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **10**, 1592

AS-TuP-14 Theoretical Investigation on Impurity Formation Mechanism During Area-Selective Atomic Layer Deposition Using Organic Inhibitors, Jiwon Kim, B. Shong, Hongik University, Republic of Korea

Recent advancements in semiconductor devices aim for performance improvement through miniaturization and also employing of threedimensional architectures. Atomic layer deposition (ALD) is often employed for its advantages of high uniformity and conformality of the deposited thin films. Area-selective ALD (AS-ALD), a potential bottom-up approach for selfaligned fabrication of thin films, may offer process innovations that can solve fabrication challenges. Furthermore, ALD on high aspect ratio (HAR) substrates often involves challenge in conformality. It was recently shown that spatial modulation of the ALD growth rates by adsorption of inhibitors with gradient in density can enhance the conformality within the HAR structures. However, in such AS-ALD approaches, molecular inhibitors are often utilized to selectively deactivate the growth of thin films, which may result in increased impurity levels if unwanted side reactions occur. In this study, possible side reactions during AS-ALD of silicon nitride (SiNx) using organic small molecule inhibitors (SMIs) are investigated utilizing density functional theory (DFT) calculations. Complete removal of surface passivation group through reaction with the reactants is crucial for the deposition of thin films without carbon impurities. However, nitride materials such as SiNx often require high process temperature for thermal ALD, at which decomposition of precursors or inhibitors can occur. Then, the highly reactive chemical species resulting from the thermal decomposition can result in non-selective deposition regardless of surface inhibition. Furthermore, such reaction can result in formation of carboncontaining surface mojeties that are significantly stable and resistant against removal, possibly leading to increased amount of carbon impurities. Therefore, our study suggest that the side reactions should be carefully considered for AS-ALD using SMIs.

AS-TuP-15 Using ALD Precursors as Inhibitors During Area-selective ALD, Marc Merkx, P. Yu, S. van der Werf, A. de Jong, E. Kessels, Eindhoven University of Technology, Netherlands; T. Sandoval, Universidad Tecnica Federico Santa Maria, Chile; A. Mackus, Eindhoven University of Technology, Netherlands

In the pursuit to develop area-selective ALD processes with a high selectivity, the main question that needs to be answered is how to effectively block the adsorption of ALD precursors on the areas where deposition is not desired. One of the most studied instances of precursor blocking is self-limiting precursor adsorption during ALD, i.e., precursor adsorption is blocked when the surface is saturated by precursor adsorbates. To exploit this knowledge, the field of area-selective deposition is exploring the use of plasma-assisted ALD precursors (i.e. precursors that do not deposit material when exposed to a thermal co-reactant) as inhibitors for selective thermal ALD processes.[1,2] However, it can be expected that not all ALD precursors block precursor adsorption equally well. By studying the blocking mechanisms of ALD precursors against other precursor chemistries, important insight can be gained into how to design or select effective inhibitor molecules for area-selective ALD. In this contribution, we systematically study the blocking of ALD precursor adsorption by another ALD precursor molecule for a range of different precursor chemistries as a model system for precursor blocking.

To study the blocking efficiency of ALD precursors, a three step (i.e. ABCtype) ALD cycle was employed. During steps A and B, precursor 1 and precursor 2 are sequentially dosed, such that precursor 2 should be largely blocked by precursor 1. Finally, in step C, O_2 plasma is used as the coreactant to remove all precursor ligands from the surface. The fraction of material that is deposited by precursor 2 in the resulting film was measured by x-ray photoelectron spectroscopy (XPS) and used as a metric for how effective precursor 1 can block precursor 2. Precursor blocking was studied for bis(diethylamino)silane (BDEAS), tetrakis(dimethylamino)titanium (TDMAT), tert-butylimidotris(dimethylamino)tantalum (TBTDMT). tris(dimethylamino)cyclopentadienylhafnium (HvALD). and trimethylaluminum (TMA). In general, it was observed that precursors that were effective at blocking precursor adsorption as precursor 1 were also difficult to be blocked when used as precursor 2, and vice versa. In addition, it was found that a CH_x termination is preferred over alkylamino termination for effective precursor blocking. In this contribution, the role that packing, reactivity, and ligand chemistry play in precursor blocking will be discussed.

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AS-TuP-16 Effect of N2 Co-Flow During Area-Selective Atomic-Layer-Deposition of Al₂O₃, *Sangjun Lee*, Sungkyunkwan University (SKKU), Republic of Korea; *C. Park, Y. Choi, S. Jeong, S. Hong*, Sungkyunkwan University, Republic of Korea; *Y. Cho, H. Lee*, *H. Kim*, *A. Klipp*, BASF, Republic of Korea; *P. Yoo*, Sungkyunkwan University, Republic of Korea; *H. Kim*, Sungkyunkwan University (SKKU), Republic of Korea

In semiconductor device manufacturing, accurate alignment of fine patterns is crucial for optimizing the chip's overall performance. Edge placement error (EPE), which occurs during the via forming process in backend-of-line metal wiring, leads to increased parasitic capacitance and degrading the reliability and performance of the device [1, 2]. To address this issue, area-selective deposition of dielectric films emerges as a possible solution. This technique selectively elevates the interlayer dielectric or intermetal dielectric between neighboring metal lines, thereby minimizing potential conductive paths and effectively reducing RC delays [3].

In this study, we enhanced the selectivity of Al2O3 atomic layer deposition (ALD) on dodecylphosphonic acid-treated Cu substrates by co-flowing N2 during Al-precursor (trimethylaluminum) injection. The selectivity significantly increased as the N2 flow rate was increased from zero to 200 sccm, prompting the utilization of various characterization techniques to determine the origin. Contact angle measurements were taken to compare the blocking capability of the self-assembled monolayer when exposed to both the precursor and N2. The selectivity was evaluated by X-ray florescence and X-ray photoelectron spectroscopy analyses. Additionally, possible changes in the dielectric constant of the Al2O3 film were examined by electrically characterizing the capacitors fabricated with Al2O3 films deposited using various N2 co-flow rates.

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AS-TuP-17 Selective Growth Mechanisms in Nickel-based Systems using Ni(tbuDAD)₂, Gabriele Botta, BRTA nanoGUNE, Italy

Nickel is an abundant and versatile element whose presence can be found in virtually every field of academic research. In fact, whether as a metal or as a compound, it exhibits properties that make it compatible with various applications such as catalysis, energy, data storage, and the aerospace industry. In ALD, the direct deposition of nickel metal has been achieved using several precursors such as Ni(Cp)2 or Ni(dmamp)2. However, for the deposition of metallic nickel, almost all ALD processes require harsh processing conditions, involving strong reducing agents such as hydrogen or ammonia, high temperatures, and/or plasmas.

One exception to this trend was proposed in 2018 by Kerrigan et al. from the group of C. Winter, who demonstrated direct nickel deposition using bis(1,4-di-tert-butyl-1,3-diazadienyl) nickel (Ni(tbuDAD)2). This process was not only performed at temperatures as low as 160°C and in the absence of strong reducing agents, but it was also found to be area-selective on metallic surfaces.

In this work, we investigated the area-selective growth mechanisms of nickel films using Ni(tbuDAD)2 and tert-butylamine on different substrate types, including metals and metal oxides as well as thermal silicon dioxide and quartz. Using surface-sensitive techniques, we characterized the

substrates before and after ALD, elucidating the key mechanisms behind nickel nucleation on growth and non-growth areas. Through high-resolution imaging and elemental mapping, we have been able to directly observe the selective coating of metallic nanostructures with nickel thin films.

Thanks to this study, we have established novel guidelines for the utilization of this chemistry for advanced area-selective purposes, raising new questions and challenges to be shared with the ALD community.

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