Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuM
Surfaces and ASD

Moderators: Dr. Jeffrey W. Elam, Argonne National Laboratory, Dr. Adrie Mackus, Eindhoven University, Netherlands

8:00am **AS1-TuM-1 Advances in the Industrial Adoption of Selective ALD Processes*, David Thompson,*** Applied Materials, Inc. **INVITED**

Since the initial adoption of atomic layer deposition in capacitor dielectrics for DRAM, and for gate dielectrics in logic at 45 nm, ALD has played a transformative role in enabling a wide variety of integration, without which the industry would have been unable to scale.However, over the last 15 year the number of steps required to process a chip has dramatically increased and integration has become increasingly complicated.

Selective deposition can offer enabling and/or simplified integration approaches, and while there has been strong adoption of some selective processes (e.g. selective epitaxy of Si and selective capping of copper with CVD Co), there remains a tremendous opportunity for the industry to solve many integration problems with selective ALD processes.

This talk will focus on several high value problems that can be addressed by selective ALD, and the additional steps required to enable these selective processes.A specific case study on leveraging selective ALD to enable higher chip speeds through reducing RC delays by leveraging an integration scheme enabling selective ALD TaN will be examined.In this particular case, the selective barrier can reduce via resistance by >50% with no reliability degradation.

Finally, the lessons learned in enabling the selective ALD TaN process will be highlighted as they relate to enabling the many other selective ALD applications that promise to continue enabling device manufacturers roadmaps.

8:30am **AS1-TuM-3 Control of Silanol Density in Silicon Oxide Surfaces via Gas-Phase Treatments to Control Metal Atomic Layer Deposition*, Mohammed Alam,*** University of California at Riverside*; F. Zaera,* University of California - Riverside

Controlling the deposition of metal films grown on oxides by atomic layer deposition (ALD) requires stringent control over the surface nucleation sites, typically hydroxyl groups. The hypothesis driving this project is that preliminary surface modification steps may be used to alter the hydroxyl surface density and with that, the properties of the ALD metal films. In the case of area-selective ALD, for example, the use of surface modifiers such as silylation agents has been implemented to deactivate all silanol sites on the non-growth surface in order to spatially direct film deposition onto the growth surface. The extent of silylation may also be controlled to tune the ALD in terms of the film density. Partial silylation can help deposit metal nanoparticles of varying sizes by immobilizing them thereby preventing their aggregation and sintering at high temperatures.

The medium in which surface modification reactions, such as silylation, are carried out in is vital to achieve control over the efficiency of the process of blocking nucleation sites. A liquid-phase environment affords little control over the surface modification process and may result in the formation of defects within the organosilane layer. These drawbacks may be eliminated by conducting the modification step in the gas phase, as was tested in this work.

In our XPS study, Si-OH sites in silica surfaces were blocked in a controlled fashion via gas-phase silylation using *N,N*-dimethyltrimethylsilylamine. The silylation efficacy was assessed by evaluating the kinetics of metal oxide ALD on the resulting substrates. The results from gas-phase silylation were compared to a set of experiments in which the modification step was performed in the liquid-phase. In both cases, the SiO_x/Si(100) surface becomes fairly unreactive during the initial stages of TiO_2 or HfO_2 ALD and remains passivated up to 5 TiO_2 cycles; the passivation is less effective with HfO_2. Nucleation sites are eventually re-activated with increasing cycles, but partial surface passivation is maintained up to 50 cycles. These results suggest that the metal precursor can eventually chemisorb onto defect sites in the silylated layer after sufficient interaction with the surface, propagating film growth. Moreover, as the results obtained with gas- vs. liquid-phase silylation are comparable in terms of ALD passivation, it is concluded that there is an intrinsic limitation to the degree of passivation achievable using this surface modification scheme. Finally, preliminary NMR results with porous silica indicate that the extent of silylation can be tuned to modify the ratio of free vs. capped nucleation sites.

8:45am **AS1-TuM-4 Inherently Area-Selective Atomic Layer Deposition of Device-Quality $Hf_{1-x}Zr_xO_2$ Thin Films through Catalytic Local Activation*, Hyo-Bae Kim,*** *J. Lee, W. Kim, J. Ahn,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD) has attracted tremendous interest as an alternative bottom-up patterning process to implement versatile fabrication of selectively formed thin films in both vertical and lateral direction in extremely downscaled 3D semiconductor devices. In this study, we report a methodology for achieving inherently selective deposition of $Hf_{1-x}Zr_xO_2$(HZO) thin films by catalytic local activation not only on noble metal surfaces like Ru and Pt, but also on the TiN surfaces. For achieving selective deposition on metal surfaces, O_2 gas was utilized as a mildly oxidizing co-reactant and cyclopentadienyl-tris(dimethylamido)hafnium(zirconium) precursors ($Hf(Zr)[Cp(NMe_2)_3]$) which require strong oxidizing agents were used to deposit HZO thin films. As a results of catalytic dissociation of O_2 molecules, we successfully achieved inherent selectivity greater than ~7 nm on both blanket Ru substrate and Pt/Si patterned substrates. Furthermore, it was demonstrated that the anti-ferroelectric HZO thin films with high dielectric constants of 31 and 34 can be fabricated selectively on TiN and Ru substrate, respectively, through the inherent AS-ALD method using catalytic local activation and ozone post-treatment. It should be noted that this intriguing approach for achieving inherent selectivity expands the potential utility of bottom-up nanopatterning processes for next-generation nanoelectric applications.

9:00am **AS1-TuM-5 Targeted Dehydration as a Route to Site-Selective Atomic Layer Deposition at TiO_2 Defects*, Jessica Jones,*** *E. Kamphaus, A. Martinson,* Argonne National Laboratory

Distinct reactivity of unique atomic arrangements (i.e. defects) on material surfaces allows for selective surface chemistry exclusively at those sites. We present an atomic layer deposition (ALD)-based technique of site-selective ALD (SS-ALD) targeting undesirable defect sites. Defects on the TiO_2 and other oxidized surfaces affect the electronic properties, interfaces, and performance of devices utilizing those interfaces. We present first principles calculations to predict the difference in hydration/hydroxylation of pristine TiO_2 terraces and minority atomic configurations including step edges and oxygen vacancies. In situ ellipsometry reveals the nucleation behavior of SS-ALD at process conditions precisely tuned for selective hydroxylation of surface defects. An island growth model for nucleation and atomic force microscopy (AFM) imaging are consistent with a site-selective growth mechanism that depends on defect density.

9:15am **AS1-TuM-6 Inhibitor-Free Area Selective Atomic Layer Deposition based on Atomic Layer Nucleation Engineering and Surface Recovery with a Feature Size of Nearly 10 nm*, Yu-Tung Yin,*** *C. Chou,* National Taiwan University, Taiwan*; W. Lee, C. Chuu,* TSMC, Taiwan*; C. Hou,* Academia Sinica, Taiwan*; T. Wang,* National Taiwan University, Taiwan*; J. Shyue,* Academia Sinica, Taiwan*; M. Chen,* National Taiwan University, Taiwan

While conventional photolithography faces more and more challenges to follow the progress of aggressive semiconductor scaling, area-selective atomic layer deposition (AS-ALD) has become a promising technique that can directly reduce the number of lithography and etching processes. In this study, novel concepts including the “atomic layer nucleation engineering (ALNE)” and “surface recovery (SR)” techniques, were proposed for the realization of AS-ALD without using any inhibitors. The AS-ALD process based on ALNE and SR results in nearly 100% selectivity of the oxide (Al_2O_3) and nitride (AlN) deposition between the dielectric (SiO_2) and the metal (Pt or W). For ALNE, by directly introducing the radio-frequency (RF) substrate bias after the exposure and purging of precursors in each ALD cycle, the difference in the binding energy of the precursor adsorbed on dielectric and metal surfaces give rise to the selectivity of film deposition. The relatively lower binding energy of the precursor on the metal surface, as compared with that on the dielectric surface, opens a processing window for the local substrate plasma to remove the precursor adsorbed on metal, which contributes to the inhibitor-free AS-ALD between SiO_2 and Pt. Furthermore, for those metals that are easily oxidized during the oxide deposition, the SR technique (i.e., by introducing the RF substrate bias again) is subsequently applied to dispose of the oxidized layer on the metal surface. Accordingly, the ALNE method achieves the high-selectivity AS-ALD over 100 ALD cycles for Al_2O_3 and AlN between the SiO_2 and Pt surfaces. For tungsten (W) which is easily oxidized during the exposure of oxidant in the ALD process, the AS-ALD of Al2O3 without any selectivity loss over 100 ALD cycles is realized between the SiO2 and W surfaces. In addition, the AS-ALD

process based on the ALNE and SR treatments has been further demonstrated on the SiO_2/W patterned substrates with the scaling of the feature size from 75 µm to ∼10 nm. In conclusion, the concept of ALNE and SR has realized the inhibitor-free AS-ALD with high selectivity, which is substantially beneficial to further extension of Moore's Law.

9:30am **AS1-TuM-7 Dopant-selective Choreography of Metal Deposition for Bottom-up Nanoelectronics***, **Nishant Deshmukh**, D. Aziz, A. Brummer, S. Kurup,* Georgia Institute of Technology, USA*; M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises an unprecedented combination of performance and scalability. While current bottom-up methods can create suitable semiconductor structures, creating semiconductor-metal contacts or the gate stack of a transistor still require top-down processes. For example, contacting Si nanowire pn diodes grown with the vapor-liquid-solid (VLS) mechanism usually employs e-beam lithography, deposition, and lift-off. Here, we report a fully bottom-up approach that combines dopant-modulated surfaces, dopant-selective attachment of a self-assembled monolayer (SAM), and area-selective atomic layer deposition (AS-ALD) to direct the deposition of Pt contacts on Si. Briefly, a bifunctional undecylenic acid SAM is first blanket attached to the Si surface. Exposure to KOH removes it from heavily-doped (~10^{20} cm^{-3}) Si surfaces while it remains on lightly-doped (~10^{14} cm^{-3}) Si surfaces. Subsequent Pt ALD yields deposition primarily on the heavily-doped Si, with selectivity ratios as high as 100. X-ray photoelectron spectroscopy (XPS) studies of undecylenic acid and its monofunctional derivatives show that undecylenic acid attaches primarily through the alkene on lightly-doped Si surface. In situ oxidation of the heavily-doped Si surfaces leads undecylenic acid to bond via the carboxylic acid. This difference in attachment allows facile undecylenic acid removal from the heavily-doped surface but not the lightly-doped surface upon exposure to aqueous KOH. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies as a function of ALD cycle number reveal Pt film morphologies consistent with classic Pt nucleation and growth. The contact resistance of the resulting Pt contacts will also be presented. This work shows a method for the dopant-selective deposition of metal contacts on semiconductors, with potential use in the fully bottom-up fabrication of semiconductor devices such as diodes and transistors for hyper-scalable nanoelectronics.

9:45am **AS1-TuM-8 Effect of Surface Pretreatment to reduce the Incubation Period of Iridium Thin Film grown by ALD on the Oxide Surface***, **Myung-Jin Jung**, J. Baek, S. Lee, S. Kwon,* Pusan National University, Republic of Korea

Iridium (Ir) has low figure of merit ($\rho_0\lambda$) and high melting temperature properties, so it has been recently spotlighted as a very important copper (Cu) alternative interconnect material in next-generation semiconductor devices. In particular, in the case of depositing a thin film using atomic layer deposition (ALD) technology, it can be expected to deposit extremely thin film with conformal, uniform and excellent step coverage characteristics even in a very complex structure or a trench structure of several nm dimension due to the inherent self-limiting characteristic of ALD. In this regard, ALD-Ir is considered as one of the most suitable metallization process for the application of advanced semiconductor interconnects. Therefore, considerable efforts have been conducted to develop a reliable ALD-Ir process having improved film qualities. And, ALD-Ir process with excellent thin film properties such as low electrical resistivity and negligible oxygen impurities was recently reported using Tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$, TICP) precursor and oxygen [1]. However, in the case of this TICP precursor, it was difficult to deposit extremely thin and continuous Ir films on the hydroxyl-terminated oxide layer due to its long incubation delay.

Therefore, in this study, a method for depositing a very thin, uniform and continuous ALD-Ir thin film with low resistivity even on oxide materials was explored by reducing the incubation period and promoting nucleation using various surface pretreatment conditions. In addition, the nucleation behavior as well as film properties of ALD-Ir on the oxide material were systemically compared and analyzed according to the surface pretreatment conditions, and finally, ALD-Ir thin film with excellent properties on the oxide surface was obtained.

References

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

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

Moderator: Prof. Dr. Stacey Bent, Stanford University

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

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

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

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

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

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

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

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

The RAIRS spectra show that aniline undergoes catalytic surface reactions for substrate temperatures above 250 °C. These reactions turn the adsorbed aniline into C_6H_x adsorbate species, while NH_3 and potentially H_2

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

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

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

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

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

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

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

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

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

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

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

References:

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

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

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

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

Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuA

Polymers

Moderator: Prof. Han-Bo-Ram Lee, Incheon National University

1:30pm **AS1-TuA-1 The Role of Co-Reactant Reactivity and Surface Passivation During Cu-Doping of NiO ALD**, ***Matthias Minjauw,*** Ghent University, Belgium; *B. Vermeulen,* Ferroelectric Memory Company, Germany; *A. Illiberi,* ASM, Belgium; *V. Sharma,* ASM Microchemistry Ltd., Finland; *M. Givens,* ASM, Belgium; *J. Dendooven, C. Detavernier,* Ghent University, Belgium

P-type transparent conducting oxides are of high interest for applications in electrocatalysis, optoelectronics, and sensing. Nickel oxide is a viable candidate owing to its chemical stability, wide band gap and excellent transparency in the visual spectrum. However, as for most applications the hole conductivity of NiO is too low, it needs to be increased by doping the NiO with metal cations such as Al, Cu, Co or Zn.[1,2] ALD has proven to be a suitable method for the growth of ultra-thin, precisely doped transition-metal-oxide films on nanostructured devices.
In this work we demonstrate ALD growth of Cu-doped NiO, using the bis(N,N'-di-t-butylacetamidinato)nickel(II) and bis(dimethylamino-2-propoxy)copper(II) precursors. For the $Ni(tBuAMD)_2$-precursor, NiO ALD growth has been demonstrated with H_2O as a co-reactant at 150°C.[2] For the $Cu(dmap)_2$-precursor, using H_2O as the co-reactant at 150°C leads to Cu_2O growth, while using O_3 leads to CuO growth at temperatures of 110°C-175°C.[3] Cu-doped NiO ALD was attempted by combining the two water-based processes in a super-cycle approach. Although the individual NiO and Cu_2O processes display growth rates compatible with literature reports (0.028 and 0.019 nm/cycle resp.), combining both processes in a super-cycle decreases the growth rate significantly (Fig. 1). In vacuo XPS experiments revealed that NiO growth is inhibited on an ALD Cu_2O surface, with negligible deposition even after 145 NiO ALD cycles (Fig. 2). By exposing the Cu_2O to ozone, NiO growth can be initiated from the initial ALD cycles. The effect of this O_3-exposure is two-fold: the Cu_2O is oxidized to CuO, and persistent carbon and nitrogen species are removed from the surface. As exposure of the O_3-treated CuO surface to a single pulse of $Cu(dmap)_2$ blocks NiO growth, but doesn't change the oxidation state of the CuO surface, it must be the $Cu(dmap)_2$ surface ligands themselves that cause the NiO growth inhibition. This is backed up by the fact that there are no ALD NiO literature reports combining $Ni(dmap)_2$ with H_2O. Finally, we demonstrate that Cu-doped NiO ALD growth can be achieved by combining the O_3-based processes in a super-cycle approach, with a growth rate comparable to the growth rates of the unit processes (Fig. 1).

1:45pm **AS1-TuA-2 Elucidating the Role of Functional Groups of Ligands for Selective Metal Blocking via Vapor-Phase Sam Deposition**, ***Chandan Das,*** Applied Materials Inc., Singapore; *B. Bhuyan,* Applied Materials Inc.; *Z. Li, J. Wu,* National University of Singapore; *J. Sudijono,* Applied Materials Inc., Singapore; *M. Saly,* Applied Materials Inc.

One of the key areas of area-selective atomic layer deposition (AS-ALD) that the industry is looking for, is the development of fully self-aligned vias (FSAV) for BEOL applications in the advanced nodes. The current study demonstrates the development of ligands possessing suitable volatility for vapor phase SAM growth, additionally being selective to the metals and not on dielectrics. While considering selectivity to the metals by specific azide-, and organophosphorus-based head groups, the tail length and head functional groups have been carefully modified as shown in Fig 1 and 2 (ESI), for delivering the ligands to the chamber for vapor phase SAM growth. Out of various ligands, L_n has shown promising selectivity (WCA ~104°) on metals compared to the SiO_2/Si (WCA ~65°) at 200 °C growth temperature [Fig 3, ESI]. The SAM grown samples have further been annealed up to 300 °C in the presence of organometallic precursors to check the stability under deposition conditions. No loss in the WCA indicates promising stability of Ln SAM, which would be a potential candidate for selective deposition at a relatively higher temperature.

2:00pm **AS1-TuA-3 Integrating Area-Selective Ald with Electrohydrodynamic-Jet Printing to Enable Additive Nanomanufacturing**, ***Tae Cho,*** *N. Farjam, T. Newsom, C. Allemang, R. Peterson, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

The demand for customizable micro/nanoscale patterning of functional materials has led to a strong interest in bottom-up manufacturing of electronics. The current state-of-the-art in fabricating functional devices includes multiple deposition and etching steps in a resource-intensive cleanroom environment. There is yet no universal manufacturing technique that can enable low-cost, high-resolution/quality, and high-throughput additive nanomanufacturing. In this work, we demonstrate the versatility of area-selective ALD with electrohydrodynamic jet (EHD) printing to pattern functional materials and manufacture fully functional devices without the traditional lithographic process.

EHD printing is an additive manufacturing technique which has been previously used to deposit functional materials with solution inks. The printing is performed at atmospheric conditions, and provides an unparalleled combination of high spatial resolution (sub-micron), fast printing speeds, and low cost. However, the materials that can be printed are limited by the solution inks, which are mostly used to print polymers. In this work, we combine EHD printing with ALD in three different manufacturing methods to pattern functional materials: additive and subtractive area-selective ALD (AS-ALD), and acid-based subtractive printing of ALD films. As shown in Scheme 1, ALD films are selectively grown by EHD printing of inhibitors on the surface. We printed polyvinylpyrrolidone (PVP) ink to "passivate" the surface and N-methyl-pyrrolidone (NMP) solvent ink to "activate" the surface towards ALD growth. This enabled additive and subtractive printing with an average linewidth of 312 nm and 9 µm, respectively.

In addition to directly patterning the polymer inhibitors, we also introduce a new subtractive printing process using acid-based inks to directly pattern the metal oxide films deposited by ALD. For this work, we patterned 50 nm thick ZnO ALD by EHD printing acid-based ink to achieve sub-10 µm resolution [2]. Various ink compositions were tested to study the etch and evaporation rates. The printed ALD ZnO features were examined using scanning electron microscopy and atomic force microscopy. Using these integrated techniques, a bottom-gate thin-film transistor (TFT) with an ALD zinc-tin-oxide (ZTO) channel was fabricated without any lithography process [1,3]. This new additive micro/nanomanufacturing platform can enable flexible and customizable patterning of metal oxides without the need for traditional lithography.

2:15pm **AS1-TuA-4 Enhanced ALD Nucleation on Polymeric Separator for Improved Li Batteries**, ***Giulio D'Acunto,*** *S. Shuchi, M. Mattinen, S. Bent,* Stanford University

Lithium batteries are the preferred choice of power sources for portable devices, electric vehicles, and energy storage due to their high energy density. However, despite their widespread use, Li batteries still have several limitations: low thermal stability, limited cycle life, and capacity decay, to name a few. To improve the efficiency of the Li batteries, ongoing research is conducted in several areas, such as battery design and active modification of well-established components. One specific area of focus is the separator, a critical element of all batteries. Its role is to separate the positive and negative electrodes while allowing ion transport.

In this study, separators, which have drawn attention due to their crucial impact on safety and good electrochemical performance, are modified by ALD Al_2O_3 to enhance thermal stability and increase the cycle life of batteries. After optimizing the surface pre-treatment, Al_2O_3 deposition is performed with trimethylaluminum (TMA) and water at 80 °C, below the shrinkage temperature of the separator, with a long exposure time and on a custom-made reaction bed, allowing uniform and conformal deposition all around the separator.

A Celgard 2325 separator - polypropylene (PP)/polyethylene (PE)/PP - is modified using different exposure times of UV ozone (UVO) to functionalize the inert carboxyl group. X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), and scanning electron microscopy are used to characterize the membranes and test the effectiveness of the UVO functionalization as well as its role in the nucleation of Al_2O_3. Moreover, electrochemical measurements, such as Li-ion conductivity and long-term cycling tests on Li|Cu half-cells, are performed.

The more hydrophilic nature of the membrane after ozone treatment, which saturates after 4.5±1.0 min of exposure to UVO, is confirmed by XPS and WCA. The thickness of ALD Al_2O_3, with 20% $Al(OH)_3$, strongly correlates to the oxygen content present on the membrane after UVO exposure. The deposition on the polymeric separator also leads to a notably lower growth rate (0.8±0.2 Å/cycle), in contrast to the well-established 1.1 Å/cycle determined on SiO_2.

Overall, we show how a controlled UVO pre-treatment can enhance the growth of ALD Al_2O_3 on the separator. We also show that adding ALD Al_2O_3 can improve battery cycle life. The resistive Al_2O_3 overlayer does not affect the Li-ion conductivity of the separator but improves its thermal stability. This work shows how a readily-accessible treatment can enhance the nucleation and control the deposition of a metal oxide by ALD, opening new possibilities to develop better Li batteries.

2:30pm **AS1-TuA-5 Improved Metal Selectivity via Inherent Orthogonal ASD: Polymer ASD Improves Nucleation Inhibition for Metal ASD***, **Hwan Oh**,* North Carolina State University, Republic of Korea*; H. Margavio,* North Carolina State University*; H. Yang,* North Carolina State University, Republic of Korea*; G. Parsons,* North Carolina State University

Despite recent achievements in area-selective deposition (ASD), the current focus on ASD is limited to single-material ASD. The integration of discrete ASD processes into a sequential process, *i.e.,* multi-material ASD has great potential to provide additional leeway in fabricating semiconductor devices.[1] Specifically, combining organic and inorganic ASD processes in an orthogonal sequence, in which the organic ASD layer can act as a sacrificial layer, can extend the functionalities of individual ASD processes. In this work, we demonstrate a multi-material ASD using individual inherent ASD processes in an orthogonal sequence: 1) poly(3,4-ethylenedioxythiophene) (PEDOT) ASD on SiO_2*vs.* Si-H [2] *via* oxidative chemical vapor deposition (oCVD) using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as an oxidant, and 2) W ASD on Si-H *vs.* SiO_2 [3] *via* atomic layer deposition (ALD) using tungsten hexafluoride (WF_6) and highly diluted silane (2 wt% SiH_4 in Ar). Herein, PEDOT ASD on SiO_2 (*vs.* Si-H) serves as a potential sacrificial layer to inhibit undesired nucleation of W on SiO_2. The cross-sectional scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) analyses show that without a pre-deposited PEDOT layer on SiO_2, 10 cycles of W ALD result in ~ 7.7 nm of W ASD on Si-H with growth per cycle (GPC) of 7.7 Å/cy, but the formation of undesired W nuclei (*i.e.,* selectivity loss) is also observed on SiO_2 (Figure 1a and 1b). On the other hand, with a pre-deposited PEDOT layer on SiO_2, the same W ALD process leads to similar growth of W ASD on Si-H, but no growth of W is confirmed on SiO_2 (Figure 1c and 1d). This result indicates that pre-deposited PEDOT (first ASD) can improve the selectivity window of W (second ASD) by inhibiting unwanted nucleation of W. This study can be extended to other material pairs or other multi-material configurations. For example, a polymer ASD can be achieved on metal (*vs.* dielectric) for another subsequent ASD of interest, such as low-k ASD on dielectric (*vs.* metal). Overall, weanticipate that multi-material orthogonal ASD canbring a new paradigm to future microelectronics manufacturing beyond sing-material ASD processes.

2:45pm **AS1-TuA-6 Self-Aligned Patterning by Area-Selective Etching of Polymers and ALD***, V. Lasonen, C. Zhang, M. Vehkamäki, A. Vihervaara,* University of Helsinki, Finland*; L. Mester,* attocube systems AG, Germany*; M. Karimi,* AlixLabs AB, Sweden*; Y. Ilarinova,* AlixLabs, Sweden*; R. Jafari Jam, J. Sundqvist,* AlixLabs AB, Sweden*; **Mikko Ritala**,* University of Helsinki, Finland

We have recently presented area-selective etching of polymers as a new approach for self-aligned thin film patterning [1]. The area-selective etching is based on different catalytic properties of surfaces under the polymer film being patterned. When annealed at a proper temperature in presence of a proper etching gas, the polymer is decomposed away from catalytically active surfaces whereas on catalytically inactive surfaces the polymer remains. The process is made possible by the small etching gas molecules (O_2 and H_2) being able to diffuse through the polymer layer and become activated by the catalytic surface. With some catalyst - polymer combinations no etching gas is needed as the polymer decomposition occurs by catalytic thermal cracking.After the self-aligned patterning of the polymer, it may remain as part of the device or, more likely, used as the growth directing template in various deposition processes, such as area-selective ALD and CVD, and line-of-sight PVD followed by lift-off.

A critical question is how accurate line edges can be made with the area-selective etching process. An obvious concern is that spill-over of activated etching gas atoms or polymer flow can blur the interface between the decomposed and non-decomposed polymer area. In this research we have explored the capabilities of the method by using about 100 nm diameter metal dots as the starting pattern. These dots were made by a lift-off process using Talbot displacement lithography and electron beam evaporation. Polyimide deposited by molecular layer deposition and poly(methyl methacrylate) (PMMA) deposited by spin coating were used as polymers. Nano-FTIR spectroscopy verified accurately defined selective removal of PMMA from Pt. After the area-selective removal of the polymers from the Pt dots, ALD Ir and Ni processes were conducted. In the case of Ir, perfect area-selective deposition was achieved, while the nickel process resulted in some scattered deposition also on the polymer but these nuclei were removed upon removal of the polymer.

Reference

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Area Selective ALD
Room Evergreen Ballroom & Foyer - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 iCVD Polymer as Inhibiting Layer for the Area-Selective ALD of Transparent Conducting Oxide Thin Films*, R. Feougier, C. Guerin,* ***Vincent Jousseaume,*** Univ. Grenoble Alpes, CEA, LETI, France

Transparent semiconductor oxides and transparent conducting oxides (TCO) are of critical importance for the development of thin-film transistors. TCO are also used as transparent electrodes for optoelectronic devices and microdisplays. In order to facilitate the integration of TCO that are difficult to pattern with standard lithography and etching processes, area selective deposition (ASD) is investigated. One approach consists in using self-assembled monolayers or polymeric films that can act as ALD inhibiting layers and prevent deposition in certain areas. For the introduction of this process in the microelectronic industry, one of the challenges is to deposit a sufficiently dense and stable inhibiting layer, preferably by a vacuum-based process.

In this work, polymeric thin films deposited by initiated chemical vapor deposition (iCVD) were evaluated as potential inhibiting layers for the AS-ALD growth of transparent conducting oxides such as ZnO and SnO_2. iCVD is a vacuum-based deposition technique that allows a very good control of polymer thickness (down to nanometer) with low roughness, on large substrates. TCO films were deposited on different polymer layers by low-temperature ALD, and the film growth and material structure were analyzed with several characterization techniques including ellipsometry, X-ray reflectometry, atomic force microscopy and time-of-flight secondary ion mass spectrometry. It is shown that poly(neopentyl methacrylate) (P(npMA)) is a very good inhibiting layer for ALD growth of zinc oxide deposited from diethylzinc and water. For example, 12 nm of P(npMA) allows to inhibit up to 100 nm of ZnO. This work shows that the same iCVD polymer can also inhibit ALD growth of SnO_2 deposited from tetrakis(dimethylamino)tin and H_2O_2. The need for a minimum polymer thickness due to the possible diffusion of the precursor in the polymer layer is also highlighted. This solution appears to be a promising alternative to self-assembled monolayers and constitutes a new path toward the implementation of ASD for the fabrication of innovative thin-film transistors, for TCO-based channels as well as for electrodes.

AS-TuP-2 Direct Patterning of ZnO Deposition by Atomic-Layer Additive Manufacturing Using a Safe and Economical Precursor*, S. Stefanovic, N. Geshlaghi,* Chemistry of Thin Film Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; D. Zanders,* Inorganic Materials Chemistry, Ruhr University Bochum, Germany*; I. Kundrata,* ATLANT 3D Nanosystems, Denmark*;* ***Anjana Devi,*** Inorganic Materials Chemistry, Ruhr University Bochum, Germany*; J. Bachmann,* Chemistry of Thin Film Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Area-selective deposition (ASD) enables bottom-up nanofabrication with individual atoms as building blocks, exploiting chemical control to deliver self-aligned fabrication without dedicated lithographic steps. However, the need for (lithographically) pre-patterned substrates, which is inherent to ASD, the generation of defects outside of the desired growth area resulting from imperfect selectivity, and the limited selection of substrate materials represent limitations to applications of ASD.

To overcome these limitations, we have invented atomic-layer additive manufacturing (ALAM): a direct-patterning atomic layer 3D-printing method based on a microfluidic nozzle design which deposits lines and arbitrary patterns of materials with atomic precision using the underlying chemical principles of ALD. With respect to methods reliant on lithography, ALAM increases flexibility, reduces manufacturing cost and time, while delivering atomic resolution (on the vertical axis). The deposition chemistry of ALAM is similar to conventional ALD and all the commercially available gaseous precursors which have been used in g-ALD are compatible with ALAM. Additionally, the minimized precursor consumption of ALAM allows us to explore new reactions with precursors which are typically less preferred in ALD because of their low vapor pressure or limited reactivity.

Here, we establish ZnO ALAM using as precursors water and $Zn(DMP)_2$ (DMP = dimethylaminopropyl), which differs from the well-studied diethylzinc ($ZnEt_2$) by its lower vapor pressure and lower reactivity. Lines and patterns of ZnO deposited by ALAM are continuous, display sharp edges, and offer residual-free surfaces. The solid is crystalline and the crystallites can be either isotropically or preferentially oriented depending on the application, as chosen based on the growth conditions. The growth rate is 1.0 Å per pass at 200°C. We demonstrate the reliability and applicability of ZnO ALAM direct patterning by fabricating a metal oxide transistor and characterizing the device performance. Taken together, these results highlight how ALAM can be more flexible and facile than ASD on lithographically defined patterns, and simultaneously more economical and safer than classical ALD.

AS-TuP-3 Density Functional Theory Study on the Passivation of Oxides Surfaces by Inhibitor*, R. Hidayat,* Sejong University, Republic of Korea*; T. Mayangsari,* Universitas Pertamina, Indonesia*;* ***Khabib Khumaini****, H. Kim, W. Lee,* Sejong University, Republic of Korea

Small molecule inhibitor (SMI) has been studied extensively for area-selective deposition and seamless gapfill processes. Acetylacetone (Hacac) passivates the aluminum oxide (Al_2O_3) surface to inhibit the growth of silicon oxide (SiO_2) by plasma-enhanced atomic layer deposition (PEALD) [1]. On the other hand, ethanol (EtOH) partially passivates the Al_2O_3 surface, resulting in a decrease of growth per cycle of the ALD Al_2O_3 process by almost half [2]. However, no theoretical study compared Hacac and EtOH as SMI. Also, there has been no report on basic compounds as an SMI. In addition, there is no theoretical study to compare oxide surfaces with different acidities. In this study, we investigated the chemisorption of three types of inhibitors, alcohol, amine, and acetone, on different oxide surfaces. EtOH, diethyl amine (Et_2NH), and Hacac were selected as the SMIs. We considered three kinds of surface, SiO_2, titanium oxide (TiO_2), and zirconium oxide (ZrO_2), due to their different acidities. The density functional theory (DFT) calculations were used to study the inhibitor chemisorption, and all possible pathways were considered to understand the mechanism. We constructed and optimized the hydroxyl groups on oxide surfaces for the simulation. The reaction and activation energies of each pathway were calculated to compare the reactivity of different inhibitors. The results can provide fundamental insights into a better selection of the SMI for seamless or area-selective ALD processes. Details of the calculation results will be presented.

AS-TuP-4 Selective Deposition on Next-Generation Patterned Carbon/SiO_2 Materials*,* ***Maggy Harake,*** Stanford University*; I. Oh,* Ajou University, Korea (Democratic People's Republic of)*; S. Bent,* Stanford University

The semiconductor industry continues to display increased interest in manufacturing smaller and more complex chips, but current top-down processing technology has proven to be challenging for these next generation devices. The versatility and sequential, self-limiting nature of atomic layer deposition (ALD) can address some of these fabrication challenges. A useful extension of ALD is area-selective ALD (AS-ALD), which can be performed using several tunable strategies including inherent selectivity and surface inhibition to provide spatial control over thin-film deposition. One such strategy is the protection of the non-growth surface using self-assembled monolayers (SAMs), which are long-chained organic molecules that chemically adsorb onto a surface to create a well-packed and dense inhibiting layer, resulting in restricted ALD growth wherever the SAM is present.

This work reports on a HfO_2 AS-ALD process on C/SiO_2 patterns using two different SAMs: octadecyltrichlorosilane (ODTS) and octadecyltrimethoxysilane (OTMS). Properties of ALD-grown dielectric materials can be exploited on carbon materials and have the potential to be used in hard mask applications. The ALD precursors used for HfO_2 ALD were tetrakis(dimethylamido)hafnium and water. Plasma-enhanced chemical vapor deposition (PE-CVD) carbon, photoresist (PR), and spin-on carbon were explored as the growth surfaces. SiO_2 was studied as a non-growth surface. The two different SAMs were compared to identify if better inhibition on SiO_2 could be achieved by exploiting the differences in the siloxane head group of the SAM molecule.

Due to the subtle variability in surface chemistries of the carbon materials, results show that in addition to adsorbing on the non-growth (SiO_2) surface, the SAMs also adsorb to varying extents onto the carbon growth surface, as detected by water contact goniometer measurements. Minimizing SAM deposition on the carbon growth regions was achieved by optimizing a cleaning procedure that works for all three carbon substrates investigated. After performing 25 cycles of HfO_2 ALD (equivalent to 2.5 nm of HfO_2), selectivities approaching 100% for all three carbon materials were retained, as confirmed by x-ray photoelectron spectroscopy. Upon increasing ALD cycles, selectivities decrease, falling below 20% after 75 cycles of HfO_2 ALD on all carbon substrates. C/SiO_2 patterns are used in combination with

OTMS, and the results show that AS-ALD can be achieved in feature sizes at the submicron scale. Finally, the use of UV-ozone treatment before ALD and the selection of different ALD precursors as potential avenues to improve selectivity will be described.

AS-TuP-6 Thermal Assisted Atomic Layer Deposition of Ruthenium by Ru Precursor and O_2 as a Reactant*, Gagi Tauhidur Rahman,* Graduate School of Advanced Science and Engineering, Hiroshima University, Japan*; Y. Amamiya, K. Uesugi, A. Teramoto,* Research Institute for Nanodevices, Hiroshima University, Japan

Area-Selective Deposition (ASD) has the potential to enable self-aligned patterning schemes. Ruthenium is a promising material for next generation interconnect and so on, due to the advantages of low bulk resistivity and large work function.A study of Ru deposition on different surfaces to determine the suitable deposition conditions, which enables the demonstration of ASD of Ru film.

Fig. 1 shows a schematic time sequence of Ru ALD. The chemical name of Ru precursor is Tricarbonyl (η^4 4 -2-methylene -1,3-propanediyl) ruthenium (II) and the chemical formula is $C_7H_6O_3Ru$. The temperatures of the Ru precursor tank and the susceptor of the ALD equipment are 60 ℃ and 250 ℃, respectively. We investigated three types different surfaces; the surfaces SPM (H_2SO_4/H_2O_2 solution) and diluted HF solution, and SiO_2 film by CVD method using Tetraethoxysilane.

Fig. 2 shows Ru film thicknesses on three surfaces, where the thicknesses are converted from XRF measurement using the calibration curve. It is evident that films on SPM (-OH terminated) and SiO_2 (-O terminated) surfaces are almost the similar however the films on HF (-H terminated) are different from the previous two films. Ru thicknesses on SPMand SiO_2 surfaces are larger than that on HF surface.

In SPM/SiO_2 cases, the terminated molecules are Si and O, and O is more electronegative than Si, so these surfaces exhibit polarization. The electronegativities of H, O and Si are 2.1, 3.5 and 1.9, respectively. However, in HF case, the terminated molecules are Si and H, and they have small differences in electronegativity. The surface shows neutral characteristics. The catalytic character is also higher in HF surface rather than SPM/SiO_2 surface. We expect more deposition on HF surface than SPM/ SiO_2 surfaces. However, HF surface showed lower deposition.For those reasons we need to investigate that on HF surface less absorption occurs or the gaseous molecules go desorption after absorption. Parallelly, we have to change the deposition condition to find the fact.

We conclude this research. ALD deposition on SPM, HF and SiO_2 surfaces were successfully completed.SPM and SiO_2 surfaces showed satisfactory deposition regarding thickness while HF surface did not exhibit due to surface neutrality. The deposited Ru was ~0.13 nm per cycle.

[Acknowledgement]

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AS-TuP-7 Enhanced Deposition Selectivity of High-k Dielectrics by Vapor-Dosed Phosphonic Acid Inhibitors Combined with Selective Lift-Off*, Jeong-Min Lee,* *W. Kim,* Hanyang University, Republic of Korea

In modern technologies, misalignment issues of multi-level pattern structures arising from conventional lithographic steps have limited further device downscaling. Accordingly, area-selective atomic layer deposition (AS-ALD) has emerged as a game-changing bottom-up patterning method, which can not only eliminate such misalignment issues but provide selective deposition on desired areas with atomic-level accuracy by virtue of chemo-selective adsorption of inhibitory molecules. Concurrently, high-*k* materials are vital for nanoelectronic fabrication, among them, ZrO_2 has been considered as an ideal candidate due to its relatively high dielectric constant and wide band gap, as well as excellent thermal and chemical stability. Therefore, we report a methodology for achieving selective deposition of ZrO_2 films by surface modification through vapor-phase functionalization of octadecylphosphonic acid (ODPA) inhibitor molecules accompanied by post-surface treatment. In this work, comparative evaluation of deposition selectivity and electrical properties of ZrO_2 thin films deposited with O_3 versus O_2 reactants was performed on SiO_2, TiN, and W substrates. Through surface modification of vapor-dosed ODPA molecules, significant growth retardation against the ZrO_2 ALD process was selectively found on TiN and W, in contrast to SiO_2 substrates. With applying chemo-selectively inhibitory characteristics, we successfully demonstrate AS-ALD of ZrO_2 films on a metal/dielectric-patterned substrate. We anticipate that this approach will advance AS-ALD of high-*k* dielectrics toward the upcoming bottom-up 3D nanofabrication.

AS-TuP-10 Area-Selective Atomic Layer Deposition of Ru Thin Films Using Phosphonic Acid Self-Assembled Monolayers for Metal/Dielectic Seletivity*, Seo-Hyun Lee,* *J. Lee, W. Kim,* Hanyang University, Korea

Area selective atomic layer deposition (AS-ALD) is a promising technique for 3D nanofabrication and emerging device architectures. AS-ALD offers numerous advantages over conventioanl top-down patterning processes. This technique exploits a bottom-up additive process that selectively binds to pre-defined areas through chemo-selective interations between the substrate and molecules. In this study, we investigated the efficacy of different phosphonic aicd (PA) self-assembled monolayers (SAMs), including octadecylphosphonic acid (ODPA), octylphosphonic acid (OPA), ethylphophonic acid (EPA), and phenylphosphonic acid (PPA), for their ability to selectively block metal/dielecitrc surfaces, specifically TiN and W versus SiO2. This effectiveness of the SAM-treated surfaces was evaluated using Ru ALD as a model process for metal/dielectirc selectivity. Our results demonstrate that the PA SAMs exhibit chemo-selective adsorption on TiN and W, but their blocking quality improves with increasing alkyl chain lengths due to strong van der Waals interactions between adjacent SAMs. Notably, the ODPA SAMs showed the highest efficacy, enabling area selective ALD (AS-ALD) of Ru thin films over 15 nm on patterned TiN/SiO2surfaces.

AS-TuP-11 Area-Selective Atomic Layer Deposition on Dielectric Substrates via Selective Adsorption of Small Molecule Inhibitors*, Jieun Oh,* *H. Park, J. Lee, W. Kim,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD), surface-determined patterning of bottom-up approaches, is a key technical element compatible with the manufacture of 3D nanoelectronics. It is possible to solve the misalignment issues that occur during the lithography step through accurate pattern placement onto the desired area (referred to as the growth area). The current dominant method for AS-ALD involves using self-assembled monolayers (SAMs) to deactivate certain surface areas. However, SAMs have some drawbacks that prevent their use for sub-10 nm device applications due to their large size, making it difficult for them to be deposited on substrates by vapor phase delivery. To overcome the limitations of using SAMs, a possible alternative is to use small molecule inhibitors (SMIs) that can be delivered in the vapor phase due to their high volatility. In this work, we have demonstrated AS-ALD on dielectric substrates based on the chemo-selective adsorption of small molecule inhibitors. This work employed molecules containing a new silane as a vapor-phase surface moderator to prevent film growth during the subsequent ALD process.The chemical adsorption of inhibitors was confirmed by exploring SiO_2 as a growth area and SiN and SiON substrates as a non-growth area. Ru ALD was carried out to check the blocking capability of the inhibitor on surfaces. It is worth noting that this approach would be applicable to advance the bottom-up nanofabrication to oxide and nitride patterns for next-generation nanoelectronics.

AS-TuP-12 Inline Metrology to Characterize and Improve Process Control of Area Selective Deposition*, Ganesh Vanamu,* *W. Lee,* Nova Metrology Instruments*; R. Koret, J. Hung,* Nova Measuring Instruments, Israel*; J. Watkins, T. Stoll,* Nova Measuring Instruments

As the semiconductors industry transitions more rapidly towards integration of nanoscale three-dimensional electronic devices, the need for Area Selective Deposition (ASD) increases because self-aligned patterning with selective Atomic Layer Deposition is advantageous over conventional patterning with lithography. The selectivity in ASD is usually achieved by changing the surface chemistry in the area where film growth is either desired or not desired. ALD techniques have proven effective in controlling the adsorption of precursor molecules in specific areas on the substrate. Area-selective ALD faces challenges such as the loss of selectivity after only a few nm thick films are deposited and the extremely long-time intervals necessary to coat defect-free self-assembled monolayers. To overcome these challenges, ASD processes have recently been developed to combine selective modification deposition and selective etching. During the first deposition process, material imperfections such as different composition films are being simultaneously deposited on different material surfaces.

During device fabrication, atomic composition and thickness of the film in the desired locations - as well as unwanted residual material left over in the un-desired locations - need to be precisely monitored after the selective etch processes. This paper explores the use of Nova VERAFLEX®, an industry standard in-line X-ray Photo Spectroscopy (XPS) system measuring materials thickness and composition including bonding states in critical HVM deposition steps. VERAFLEX® measures ultra-thin films with Angstrom level resolution and sensitivity and is used for advance process control of the deposition process. XPS with automated feed forward capability, provides a precise thickness and composition of multi-layers without being affected by the properties of the underlying complex films. Compared to optical metrology solutions such as ellipsometers, XPS holds the advantage of directly detecting and analyzing atom-specific signals without the need to deconvolve optical properties from film thicknesses. For this particular ASD process, we measure the different surfaces where the ALD occurs prior to the deposition and then measure the film after the selective etch to determine the thickness and composition of the desired and unwanted materials on each of the surfaces. With fully automated inline capability on 300mm wafers, VERAFLEX® enables quick turnaround of XPS measurements, thus accelerating the development of ASD process development and help solve critical device challenges by provide better process control.

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Wang, T.: AS1-TuM-6, 1
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Yang, H.: AS1-TuA-5, 5
Yeon, C.: AS2-TuM-15, 3
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