Area Selective ALD
Room Arteveldeforum & Pedro de Gante - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Thermally Assisted Area Selective Atomic Layer Deposition*, Bart de Braaf*, TU / Eindhoven, Netherlands

In our recent published work, we explore the possibility of achieving area selective ALD by applying temperature gradients on the substrate [1]. In this approach, the majority of the substrate is kept at a low temperature, which suppresses the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modelling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized spots, as well as lines, of deposited material given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the pattern deposited on the substrate.

A practical example of this technique is the ALD process of Si_2H_6, where instead of a co-reactant the elevated temperature induced by the laser itself is used to remove the ligands [2]. For this process, it is reported that surface diffusion of deposited molecules also influences growth of the spot that is formed on the substrate. I will present new results from a model that includes this surface diffusion, and study its effect on the deposition on the substrate both at constant temperature and for the case where locally the substrate is heated by a laser. Our model suggest that the absorption rate goes up with increasing diffusivity at constant temperature.

Bibliography

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[2] Y. Suda, M. I. (1996). Ar+-laser-assisted subatomic-layer epitaxy of Si. *Journal of Crystal Growth*, 672-680.

AS-TuP-2 An Approach to the Prevention of Chemical Deterioration of Surfaces During Ex-Situ Patterning Steps*, Bernhard van der Wel, T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Atomic layer deposition (ALD), enabled by sequential self-limiting vapor-solid reactions, is a well-known technique to provide thin films with high conformality, large area uniformity and excellent film thickness control. Applying area-selective ALD (ASALD) allows for reduction of the amount of lithography and critical alignment steps during film patterning for device fabrication [1].

In this work, we propose a novel method for ex-situ thin film patterning, preventing possible chemical deterioration of the surfaces during patterning by chemicals and/or exposure to a reactive chemical ambient. This may be crucial to minimize the effect of undesired interaction of the surface with oxidants, etchants, etc. Preventing or re-establishing required chemical terminations (i.e., functional chemical groups) of the surface is needed to successfully enable a subsequent ASALD process.

After deposition of the material of interest on a substrate, it is capped in-situ (in-vacuo) by amorphous silicon (a-Si) using trisilane (Si_3H_8), protecting the film surface from subsequent possible chemical interactions. The protecting a-Si and underlying layer can be patterned ex-situ, without directly exposing the underlying film to a chemically reactive environment. This allows to prevent the surface of the underlying film from chemical modifications (e.g. by oxidation in the ambient or changing chemical termination of the surface by etching). After stripping the native oxide from the a-Si using hydrogen fluoride (1% HF), the patterned substrate is brought back to the reactor. Next, the substrate is exposed to atomic hydrogen (at-H), generated by letting H_2 interact with a heated tungsten filament, removing the silicon by forming volatile SiH_4 [2]. This opens up the initial film with the originally-present chemical terminations, favoring area-selective deposition by the next in-situ ALD step. A schematic overview of the designed process is given Figure 1, see supplemental document.

[1] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, “From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity,” Chem. Mater., vol. 31, no. 1, pp. 2–12, 2019.

[2] H. N. Wanka and M. B. Schubert, “High silicon etch rates by hot filament generated atomic hydrogen,” J. Phys. D. Appl. Phys., vol. 30, no. 8, pp. L28–L31, Apr. 1997.

AS-TuP-3 Surface Dependence and Selectivity During Atomic Layer Deposition of $Ge_2Sb_2Te_5$*, Jyoti Sinha, L. Gallis, J. Clerix,* KU Leuven, IMEC Belgium , Belgium*; L. Nyns,* IMEC Belgium , Belgium*; A. Delabie,* KU Leuven, IMEC Belgium , Belgium

The complex device architecture for Phase change Random Access Memory (PCRAM) has garnered attention towards Atomic Layer Deposition (ALD) for conformal or selective deposition. Ge2Sb2Te5 is one of the promising phase change materials which has been used in PCRAM devices. Ge2Sb2Te5 devices use either W or TiN as bottom electrode and SiO2 or SiN as isolating material for confining heat within the cell [1]. The development of selective deposition processes for such device structures benefits from insight in the growth behaviour of Ge2Sb2Te5 ALD. In this work, we therefore investigate the substrate dependence and selectivity of Ge2Sb2Te5 ALD where TiN and SiO2 were selected as substrates. GeCl2. C4H8O2, SbCl3 and ((CH3)3Si)2Te have been used as precursors to deposit Ge2Sb2Te5 by alternating GeTe and Sb2Te3 subcycles. The growth-per-cycle of Ge2Sb2Te5 ALD is 0.36 nm/cycle. Rutherford Backscattering Spectrometry (RBS) confirmed that Ge2Sb2Te5 layers of ~20 nm has the 2-2-5 composition. We observe linear ALD growth behaviour on both TiN and SiO2 substrates, indicative of fast film formation. Further, both substrates were treated with dimethylamino-trimethylsilane (DMA-TMS) to alter the surface properties for evaluating the selectivity of Ge2Sb2Te5 [2]. The DMA-TMS treatment on TiN shows minor effect on the surface composition and Ge2Sb2Te5 ALD growth behaviour. In contrast, the DMA-TMS treatment on SiO2 substantially inhibits the growth of Ge2Sb2Te5 (figure 1) and no nanoparticles are observed using scanning electron microscopy (SEM) till 64 cycles, while a Ge2Sb2Te5 layer of ~20 nm is obtained on DMA-TMS treated TiN. For higher number of cycles, nanoparticle analysis on DMA-TMS treated SiO2 indicates that growth of Ge2Sb2Te5 follows particle migration and coalescence (figure 2). Thus, the modified surface properties due to chemical treatment provides the selectivity of Ge2Sb2Te5 towards SiO2. This is confirmed by a demonstration of 20 nm of Ge2Sb2Te5 ASD in nanoscale SiO2/TiN line-space patterns.

AS-TuP-4 *In-situ* Surface Cleaning and Area Selective Deposition of SiO_xN_y film on Cu patterns using Anhydrous N_2H_4*, Su Min Hwang,* *J. Kim, D. Le, Y. Jung, K. Tan, J. Veyan,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas

Area-selective atomic layer deposition (AS-ALD) has been considered as a prominent technique due to the escalating demands for eliminating the edge placement errors with current top-down approaches in semiconductor processing at the sub-5 nm node.[1–3]. Recently, it has been reported that anhydrous hydrazine (N_2H_4) can be employed as the reduction of the Cu oxide to metallic Cu surface.[3] By employing the high reactivity of hydrazine, under the ALD environment, the metallic surface condition can be maintained, or the oxidation/reduction of the Cu surface can be repeated under the ALD environment. Eventually, area selective deposition of dielectric material (e.g., ALD-SiO_x on Si, SiN_x, TiN, AlO_x, substrates) can be achieved, whereas nucleation delay and limiting surface oxidation on Cu sample can occur.Additionally, a detailed change of Cu condition with precursor exposures will be studied using *in-situ* surface analysis.

In this study, the consecutive surface cleaning and AS-ALD of SiO_2 process was demonstrated. To identify the substrate dependence on ALD selectivity, Cu, Si, SiN_x, TiN, and AlO_x substrates were loaded in the ALD chamber at the same time. Prior to the ASD process, the samples were pretreated with N_2H_4 at 200 °C. After that, the ABC-type ALD-SiO_2 was performed. In the Si precursor half-cycle, the tris(dimethylamino)silane (step A), was exposed for 0.2 s, followed by a precursor trapping time for 120 s and purging time of 180 s. In the oxygen reactant half-cycle, the O_3/O_2gas mixture (step B), was introduced for 0.2 s and captured for 120 seconds, followed by purging the chamber with a continuous flow of N_2 carrier gas for 180 seconds. After the ALD-SiO_x cycle, an additional of surface recovery step with N_2H_4 (step C) was introduced. With five

supercycle ALD-SiO_x processes, growth of SiO_2 on both bare Si and SiN_xsubstrates, formation of metal-silicates (and/or SiO_x) on TiN_x and AlO_x suggest that the supercycle-based ALD-SiO_xprocess does not impact the growth of SiO_x on top of dielectric substrates. On the other hand, the deposited amount of SiO_x on Cu substrate is approximately 35% less than the AB-typed ALD-SiO_x process. Despite slight detection of SiO_x on Cu (non-growth) substrate, the feasibility of the ASD process with repeating surface oxidation and reduction was demonstrated. The detailed experimental results will be presented.

We thank Rasirc Inc. for funding this project and providing the Brute N_2H_4.

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[2] M.F.J. Vos et al., *J. Phys. Chem. C,* **122**, 22519 (2018).

[3] S.M. Hwang, et al., *ECS Trans*. **92**, 265 (2019).

AS-TuP-5 Inherently Area-Selective Atomic Layer Deposition of SiO_2 through Chemoselective Adsorption of an Aminodisilane Precursor on Oxide versus Nitride Substrates, ***Jeong-Min Lee**, J. Lee,* Hanyang University, Korea (Republic of)*; H. Oh, B. Shong,* Hongik University, Korea (Republic of)*; T. Park, W. Kim,* Hanyang University, Korea (Republic of)

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 work, we report a methodology for achieving inherently selective deposition of high-quality oxide thin films through chemoselective adsorption of an aminodisilane precursor, 1,2-bis(diisopropylamino)disilane (BDIPADS), on oxide versus nitride substrates. Density functional theory (DFT) calculations show higher reactivity for adsorption of BDIPADS on OH-terminated SiO_2 compared with NH_2-terminated SiN surfaces, indicating selective growth of SiO_2 films in the SiO_2 area. Applying BDIPADS precursor to both SiO_2 and SiN substrates results in inherent deposition selectivity of ~1 nm even without the use of inhibitory molecules such as self-assembled monolayers. Using this inherent selectivity as a starting point, we further enhance deposition selectivity using combined ALD-etching supercycle strategies in which HF-wet etching step is periodically inserted after 20 cycles of ALD SiO_2, leading to an enlarged deposition selectivity of approximately 5 nm after repeated ALD-etching supercycles. This approach can be envisaged to provide a practically applicable strategy toward highly selective deposition using inherent AS-ALD that can be incorporated into upcoming 3D bottom-up nanofabrication.

AS-TuP-6 Organothiol Inhibitor Instigated Area Selective Deposition of HfO_2, ***Summal Zoha**, B. Gu,* Incheon National University, Korea (Republic of)*; F. Pieck, R. Tonner,* Universität Leipzig, Germany*; H. Lee,* Incheon National University, Korea (Republic of)

With continuous progress in the field of nanofabrication and nanotechnology, the semiconductor industry has greatly flourished. However, efforts for further reduction in feature sizes of electronic interconnects in search of better and fancier devices, are still ongoing. The struggle to search for better area selective deposition (ASD) processes has led researchers to manipulate deposition surfaces using different passivation tools. In this regard, surface inhibitors have gained a lot of attention. In this study, an organothiol inhibitor has been utilized for ASD on metal, oxide, and nitride surfaces, Cu, SiO_2, and TiN, respectively. The inhibitor selectively adsorbs on the Cu and SiO_2 surfaces at 400 ºC, while the TiN surface remains unaffected after exposure to the inhibitor. Upon high-temperature exposure, the organothiol inhibitor is capable of decomposing to assist the adsorption of its different parts on the Cu and SiO_2 substrates, thereby simultaneously inhibiting two surfaces through a single inhibitor. The inhibited substrates were examined for adsorption and inhibition using surface analysis tools including water contact angle (WCA) measurements, X-ray photoelectron spectroscopy (XPS), etc. Blocking results revealed promising blocking potential against HfO_2 ALD on Cu compared to SiO_2, whereas the TiN surface did not exhibit any blocking at all. Furthermore, the surface chemistry and reactivity have been explained by theoretical calculation using the Monte Carlo method and density functional theory.

Area Selective ALD
Room Baekeland - Session AS1-WeA

Area Selective Deposition I

Moderators: Amy Brummer, Georgia Institute of Technology, Il-Kwon Oh, Ajou University

1:30pm **AS1-WeA-1 Polystyrene Brush Deactivation Layers for Area Selective Atomic Layer Deposition**, ***Caitlin McFeely**, M. Snelgrove , K. Shiel, G. Hughes,* School of Physical Sciences, Dublin City University , Ireland*; P. Yadav, M. Morris,* AMBER Research Centre and School of Chemistry, Trinity College Dublin, Ireland*; E. McGlynn, R. O'Connor,* School of Physical Sciences, Dublin City University, Ireland

Research into the field of area-selective atomic layer deposition (AS-ALD) is key for the development of new methods for the fabrication of modern microelectronics, as current technologies are reaching their limits. Typically, the selectivity originates from modifications that either activate or deactivate the substrate surface. Polymer brushes have been previously shown to act both as an activation or deactivation layer within the field of area selective deposition (ASD) [1,2]. These brushes have been widely researched due to their capacity to enable rapid fabrication, making them an industrial relevant route for processing semiconductor devices [3]. Here we focus of the use of polystyrene (PS), which is a polymer known for its ability to act as a deactivation layer for the use in ASD.

This work studies the effect that the thickness of a PS brush has on its ability to act as an effective deactivation layer against a thermal HfO_2 atomic layer deposition (ALD) process using $HfCl_4$ and H_2O as the precursor and co-reactant, respectively. Using X-ray photoelectron spectroscopy as the primary characterisation technique, our results show an increasing blocking efficacy with an increase in the PS brush thickness. The thickest PS brush, of approximately 11 nm, effectively blocked a 300 cycle ALD process which resulted in 19 nm of HfO_2 on native oxide covered Si. Due to the significantly faster fabrication times of PS brushes, this process is deemed a highly competitive alternative to the more widely used AS-ALD methodologies such as self-assembled monolayers.

(1) Snelgrove, M.; McFeely, C.; Mani-Gonzalez, P. G.; Lahtonen, K.; Lundy, R.; Hughes, G.; Valden, M.; McGlynn, E.; Yadav, P.; Saari, J.; Morris, M. A.; O'Connor, R. Aluminium Oxide Formation via Atomic Layer Deposition Using a Polymer Brush Mediated Selective Infiltration Approach. *Appl. Surf. Sci.*2020, *515*.

(2) Snelgrove, M.; McFeely, C.; Shiel, K.; Hughes, G.; Yadav, P.; Weiland, C.; Woicik, J. C.; Mani-Gonzalez, P. G.; Lundy, R.; Morris, M. A.; McGlynn, E.; O'Connor, R. Analysing Trimethylaluminum Infiltration into Polymer Brushes Using a Scalable Area Selective Vapor Phase Process. *Mater. Adv.*2021, *2* (2), 769–781.

(3) Lundy, R.; Yadav, P.; Selkirk, A.; Mullen, E.; Ghoshal, T.; Cummins, C.; Morris, M. A. Optimizing Polymer Brush Coverage To Develop Highly Coherent Sub-5 Nm Oxide Films by Ion Inclusion. *Chem. Mater.*2019, *31* (22), 9338–9345.

1:45pm **AS1-WeA-2 Area Selective Deposition of Ruthenium using a W Precursor Inhibitor**, ***Chi Thang Nguyen**, N. Trinh, M. Lee, H. Lee,* Department of Materials Science and Engineering, Incheon National University, Korea (Republic of)

Atomic layer deposition (ALD) enables the precise control of Angstrom-scale film thickness with excellent conformality due to its self-saturated surface reactions. By maximizing the surface-dependent growth, ALD could be extended to one of the patterning technologies, area selective atomic layer deposition (AS-ASD), over thin film deposition. For AS-ALD, inhibitors, such as self-assembled monolayers (SAMs), have been commonly used to deactivate surface chemical reactivity. In our group, we have proposed another opportunity of precursors, which are originally developed for thin film deposition by ALD, as an inhibitor for AS-ALD. Precursor inhibitors could have several advantages over conventional SAM inhibitors, such as high compatibility, capability for vapor phase delivery, bifunctionality, and relatively small size. In this work, we investigated a Ru ASD process usinga W precursor inhibitor which was developed for W ALD. Interestingly, it was observed that surface energy measured by water contact angle analysis was deceased with increasing exposure time which is an opposite trend to the results in ASD research. To understand the change, the adsorption energy and behavior of the W precursor inhibitor were studied by using density functional theory (DFT) calculation. A single exposure of the W precursor inhibitor layer could block the growth of Ru ALD up to 200 cycles with selectivity over 90 %.The absorption density of the W inhibitor was improved by using multi-exposure instead of continuous exposure. The results from the physical interaction simulation of the W inhibitor by Monte Carlo (MC) simulation show that the packing density of the inhibitor could be further increased by minimizing steric hindrance effects during adsorption. As a result, the blocking property of the W precursor inhibitor was improved, blocking up to 300 Ru ALD cycles.

2:00pm **AS1-WeA-3 Electron-beam Functional Group Pattering on HOPG for Area-Selective Atomic Layer Deposition**, ***Matthias Young**, G. Koerner, Q. Wyatt,* University of Missouri*; B. Bateman,* Berea College*; C. Boyle, M. Maschmann,* University of Missouri

In this work we report on a new area selective atomic layer deposition (AS-ALD) approach enabled by a spatially controlled hydroxylation process. The processing occurs within a low-pressure water vapor ambient established within an environmental scanning electron microscope (ESEM). The ESEM electron beam interacts with the water vapor and generates a local region of reactive species (e.g. hydroxyl radicals) in the vicinity of the focused electron beam. Here, we functionalize exfoliated highly ordered pyrolytic graphite (HOPG) substrates which are natively nonreactive to the ALD precursors. The electron-beam patterning process introduces reactive hydroxyls on the graphene substrate. The hydroxylated region is sufficiently stable to withstand ALD deposition temperature of 150 ^oC, and the pattern fidelity is enabling for dense selective ALD growth in the patterned area.

In the current study, hydroxyl functionalization and ALD deposition occurs along line scans and square regions of up to 2 x 2 micron in area. We show that the hydroxyl functionalization, and thus ALD deposition efficacy, is highly dependent on ambient water vapor pressure and electron beam dwell time. The hydroxyl functionalization and resulting ALD coating is characterized using atomic force microscopy and energy dispersive spectroscopy (EDS) mapping. Line widths as small as 40 nm and growth/no growth selectivity in excess of 99% are demonstrated.

2:15pm **AS1-WeA-4 Inhibitor Adsorption During Area-Selective ALD: Do Mixtures of Adsorption Configurations Lead to a Loss of Selectivity?**, ***Marc Merkx**, I. Tezsevin, P. Yu, J. Li, R. Lengers, E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Small molecule inhibitors (SMIs) are attracting interest in the field of area-selective atomic layer deposition (ALD) because of their straightforward integration into industrial process flows. However, one of the challenges is that SMIs typically adsorb in a mixture of adsorption configurations, which often are not all suited for precursor blocking. In this work, we compare two inhibitors, aniline and acetylacetone (Hacac), and study whether the different adsorption configurations can be a curse or a blessing for obtaining a high selectivity.

Aniline provides metal/dielectric selectivity (e.g. Ru versus SiO_2)[1] for area-selective ALD. Density functional theory (DFT) calculations show that aniline adsorbs either with the amine group to the surface through a δ-bond or with the phenyl ring through a π-bond. Although the δ-configuration is less strongly bonded to the Ru than the π-configuration, both are bonded sufficiently strong, resulting in a stable inhibition layer that is inert toward incoming precursor molecules. Random sequential adsorption (RSA) simulations were used to predict the coverage and packing of SMIs in saturation.[2] These simulations show that a significant fraction (~30%) of the aniline adsorbs in the δ-configuration, thereby enhancing the inhibitor coverage. In addition, the simulations predict that there are no gaps that are large enough to act as nucleation sites for precursor adsorption.

Hacac can be employed to achieve selectivity between different oxide surfaces (e.g. Al_2O_3 and SiO_2).[3] Infrared (IR) spectroscopy and DFT calculations show that Hacac adsorbs either in chelate or monodentate configuration, where both or only one of the O atoms bonds to the surface, respectively. The monodentate configuration was found to desorb due to its lower binding energy to the surface. In addition, interactions with the precursor through its unreacted C-OH/C=O group lead to displacement of the Hacac inhibitor molecules from the surface and therefore loss of selectivity. IR spectroscopy and RSA simulations show that this configuration makes up ~20% of the adsorbed Hacac in saturation, while it does not contribute to precursor blocking.

In summary, having a mixture of inhibitor adsorption configurations leads to a loss of selectivity for Hacac, while it improves precursor blocking for aniline. A mixture of configurations can therefore be beneficial or detrimental for the selectivity depending on the binding energy and orientation of each bonding configuration involved.

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

[2] Evans, *Rev. Mod. Phys.***65**, 1281 (1993)

[3] Merkx *et al., Chem. Matter*. **32**, 3335 (2020).

2:30pm **AS1-WeA-5 Area Selective Deposition for ZnO Hard Mask by 2D-like Carbon fabricated by Molecular Layer Deposition***, **Seunghwan Lee**, G. Baek, H. Yang,* Hanyang University, Korea*; T. Van, B. Shong,* Hongik University, Korea (Republic of)*; J. Park,* Hanyang University, Korea

Area selective deposition (ASD) is a promising technique as a bottom-up process for creating improved overlay or self-alignment, attaining errorless alignment, increasing yield, and reducing cost of manufacturing. The selectively grown metal or metal oxide can be employed as a robust hard mask. For bottom-up process, area selective atomic layer deposition has been researched vigorous using surface chemistry. In this research, a strategy for ASD using molecular layer deposition (MLD) is introduced, which is useful for conformal deposition of organic layer that delays film growth.

An indicone layer, which has alkoxide sturcutre, was fabricated by MLD process using INCA-1 (bis(trimethysily)-amidodiethylindium) and HQ (hydroquinone), and was thermally annealed. The atomic structures of as-dep and annealed indicone films were analyzed by XPS and Raman spectra. The indium was almost completely removed with annealing process, and carbon structure was transformed to graphitic carbon above 450 ^{o}C annealing temperature. The thermally annealed indicone was used as an inhibitor, which can delay 60 cycles of ZnO (equivalent to a thickness of about 11nm). In addition, to prove chemical mechanism of precursor adsorption on graphitic carbon, density functional theory calculations were utilized. Finally, ALD ZnO was selectively deposited on Al_2O_3/SiO_2 line pattern for interconnecting SiO_2 line pattern by transferring hard mask using RIE.

2:45pm **AS1-WeA-6 Bifunctionality of Si Precursors to Enable Area Selective Deposition of Ru and Atomic Layer Deposition of SiO_2***, **Sumaira Yasmeen**, B. Gu, Y. Kang, H. Lee,* Incheon National University, Korea (Republic of)

Area selective deposition (ASD) has enabled the growth of materials on the target areas of patterned substrates to address the existing roadblocks in the semiconductor industry. ASD is very crucial in the current era as it has shown many possible ways to enable the down-scaling of electronic devices with process simplification. Several different approaches have been used for ASD including the use of self-assembled monolayers (SAMs) and small molecule inhibitors (SMIs). However, due to the associated disadvantages like the long-chain size of SAMs, poor selectivity, and thermal degradability of SMIs, researchers have diverted their attention to the use of precursors as inhibitors. The main advantage of using precursor inhibitors is to cultivate their bifunctionality as an inhibitor for ASD and a precursor for atomic layer deposition (ALD). In other words, they can be used as precursors for specific ALDs when used with a proper counter reactant, as well as can be used as inhibitors as they do not react with the mild counter reactants. In this work, we investigated two different Si precursor inhibitors which can form SiO_2 ALD using ozone counter reactant, and also due to their chemoselectivity, they inhibit the surface towards several ALDs which require H_2O or O_2 as a counter reactant. The Si precursor inhibitors selectively adsorb on the SiO_2 surface but not on Cu, so in this way, Ru can be selectively deposited on the Cu surface. Furthermore, when used ozone as a counter reactant, it forms ALD SiO_2. Experimental analysis and electrical measurements confirmed the formation of high-quality SiO_2 film using both Si precursor inhibitors. Dielectric constant, leakage current, and O/Si stoichiometric ratio of ALD SiO_2 from both Si precursor inhibitors were found to be consistent with conventional SiO_2 ALD film. The adsorption chemistry of the Si precursor inhibitors and Ru blocking were investigated using theoretical density functional theory calculation, Monte Carlo simulations, and experimental approaches. Understanding the precursors' chemistry and physical and chemical interactions can open doors for many other precursor molecules to be used as inhibitors for the next generation nanofabrication.

3:00pm **AS1-WeA-7 TiO_2 Area-Selective Deposition: Using Selectivity Loss Mechanisms to Advance Applications in Nanopatterns and EUV Resist Materials***, **Rachel Nye**,* North Carolina State University*; K. Van Dongen,* KU Leuven, Belgium*; D. De Simone, J. de Marneffe, H. Oka,* IMEC, Belgium*; G. Parsons,* North Carolina State University*; A. Delabie,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD) is rapidly gaining interest as a bottom-up nanopatterning technique in semiconductor manufacturing to facilitate shrinking device sizes that traditionally rely on expensive and complex lithography steps. One key feature of ASD that has not been well established in literature is the amenability of processes to feature scales relevant to electronic devices (i.e. sub-50 nm patterns).[1] Additionally, there is growing industrial interest to expand ASD applications to new fields such as EUV lithography, where ASD of etch resistant layers could improve pattern resolution and reduce line-edge roughness (LER).[2]

In this work, we present a study of TiO_2 ASD that addresses both challenges: demonstrating successful ASD on 45 nm half-pitch patterns and on EUV resist materials. First, the selectivity loss mechanism of TiO_2 ALD ($TiCl_4$/H_2O at 150 ^{o}C) on dimethylamino-trimethylsilane (DMA-TMS) passivated SiO_2 is investigated. Scanning electron microscopy, Rutherford backscattering spectrometry (RBS), and kinetic modeling results demonstrate nucleation site generation during TiO_2 as the primary contributor towards selectivity loss on the TMS non-growth surface. These undesired nucleation sites are effectively mitigated with periodic etching and subsequent re-passivation of the surface, resulting in significant selectivity improvement on the growth surface (TiN) with minimal defectivity on the non-growth surface (passivated SiO_2), according to transmission electron microscopy (TEM) images (Fig. 1). The DMA-TMS inhibitor is perfectly suited for this cyclical ASD process as it passivates SiO_2 without affecting TiO_2. Furthermore, we discuss the feature size-dependence of selectivity. As a next step, we explore TiO_2 ASD on methacrylate-based EUV resist materials on the basis of EUV exposure and protecting group using RBS measurements (Fig. 2). We provide insight into selectivity loss mechanisms on the EUV resist materials and utilize this information to tune the polymer structure to induce selectivity to TiO_2 ALD for use in resist hardening or tone inversion applications.

In summary, we take a considerable step in the advancement of TiO_2 ASD using mechanistic insights to improve selectivity in both nanopatterns and EUV resists. The impact of these results may be used to advance progress of feature-scale ASD research as well as catalyze ASD applications to improve pattern resolution and LER on ultra-small EUV lithography patterns.

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Area Selective ALD
Room Baekeland - Session AS2-WeA

Area Selective Deposition II

Moderators: Stacey Bent, Stanford University, Rachel Nye, North Carolina State University

4:00pm **AS2-WeA-11 Intrinsic Area-Selective Atomic Layer Deposition of Aluminium Nitride***, **Bernhard van der Wel**, T. Aarnink, A. Kovalgin,* University of Twente, the Netherlands

Group III-V nitrides (in short III-N such as AlN, GaN, InN and their alloys) are thermally and chemically stable semiconductors suitable for use in optical and high-power electronics as their bandgaps cover a spectral range from deep ultraviolet to near infrared [1]. Fabrication of mono-crystalline III-N substrates is expensive, as well as their realization on silicon wafers, typically involving high-temperatures and thick buffer layers. Fabrication of poly-crystalline variants are a viable route to reduce fabrication costs and deposit with a low thermal budget (≤ 400 °C).

Atomic layer deposition (ALD) is well-known to offer high conformality, large area uniformity and film thickness control at sub-nm scale. Self-limiting surface reactions in ALD, requiring presence of certain chemical groups on the surface for enabling such reactions, can be beneficially utilized to achieve area-selective deposition. The latter is required to overcome critical alignment requirements during film patterning and reduce the amount of lithography steps [2].

In this work, we demonstrate inherent area-selective atomic layer deposition (ASALD) of Aluminium Nitride (AlN) films in purely thermal mode (350 °C) and at a low reactor pressure (1.5e-3 mbar), from trimethylaluminium (TMA) and ammonia (NH_3). AlN is selectively grown on patterned substrates, consisting of areas of sputtered AlN and thermal SiO_2 ranging from 2×2 μm^2 to 10×10 mm^2. Proper pre-treatment facilitates growth on the sputtered AlN. Film growth is monitored in-situ by spectroscopic ellipsometry (SE) and verified by ex-situ SE and atomic-force microscopy. After 350 cycles the film thickness on sputtered AlN is approximately 12.5 nm, whereas on the SiO2 area the thickness is less than 1 nm. The interfaces, confirming selective deposition, are examined by transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS, sputter profiling) confirmed the selectivity and showed a stoichiometric Al to N ratio with oxygen and carbon contaminations as low as 8% and 3%, respectively.

[1] D. A. Neumayer and J. G. Ekerdt, “Growth of Group III Nitrides. A Review of Precursors and Techniques,” Chem. Mater., vol. 8, no. 1, pp. 9–25, Jan. 1996.

[2] A. J. M. Mackus, M. J. M. Merkx, and W. M. M. Kessels, “From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity,” Chem. Mater., vol. 31, no. 1, pp. 2–12, 2019.

4:15pm **AS2-WeA-12 Surface-Diffusion Control Enables Tailored-Aspect-Ratio Nanostructures in Area-Selective Atomic Layer Deposition**, ***Philip Klement**, D. Anders, L. Gümbel, M. Bastianello, F. Michel, J. Schörmann, M. Elm,* Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany*; C. Heiliger,* Institute of Theoretical Physics & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany*; S. Chatterjee,* Institute of Experimental Physics I & Center for Materials Research (ZfM), Justus Liebig University Giessen, Giessen, Germany

Area-selective atomic layer deposition is a key technology for modern microelectronics as it eliminates alignment errors inherent to conventional approaches by enabling material deposition only in specific areas. Typically, the selectivity originates from surface modifications of the substrate that allow or block precursor adsorption. The control of the deposition process currently remains a major challenge as the selectivity of the no-growth areas is lost quickly.

Here, we show that surface modifications of the substrate strongly manipulate the surface diffusion. The selective deposition of TiO_2 on poly (methyl methacrylate) and SiO_2 yields localized nanostructures with tailored aspect ratios. Controlling the surface diffusion allows to tune such nanostructures as it boosts the growth rate at the interface of the growth and no-growth areas. Kinetic Monte-Carlo calculations reveal that species move from high to low diffusion areas. Further, we identify the catalytic activity of $TiCl_4$ during the formation of carboxylic acid on poly (methyl methacrylate) as the reaction mechanism responsible for the loss of selectivity, and show that process optimization leads to higher selectivity. Our work enables the precise control of area-selective atomic layer deposition on the nanoscale, and offers new strategies in area-selective deposition processes by exploiting surface diffusion effects.

4:30pm **AS2-WeA-13 Study on Area-Selective Atomic Layer Deposition of Al_2O_3 with a Series of Al Precursors**, ***Il-Kwon Oh**,* Ajou University, Korea (Republic of) **INVITED**

Area-selective atomic layer deposition (AS-ALD) offers the advantage of exploiting surface chemistry to deposit a material in a targeted area. Therefore, it may allow a reduction in the number of lithography and etch steps, resulting in lowering of errors in the patterning process as well as a decrease in manufacturing costs. For example, a self-aligned hard mask fabricated by AS-ALD can guide etching of via holes and deposition of metal wires in the metallization process to avoid shorts between metal layers.

Several metal oxide systems, such as Al_2O_3, TiO_2, ZnO, and HfO_2, have been explored for AS-ALD processes. For a hard mask, Al_2O_3 possesses advantages over other metal oxides due to its high hardness as well as chemical inertness for etching selectivity. However, despite extensive studies on ALD Al_2O_3, there are few studies on AS-ALD of Al_2O_3. Furthermore, literature suggests that Al_2O_3 may be comparatively difficult to block; for example, the blocking selectivity of Al_2O_3 is limited to only ~6 nm whereas ZnO can be blocked for over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD, which motivates the current study to elucidate the mechanism of Al_2O_3 AS-ALD based on a comparative study of Al precursors.

In this work, the recent development of AS-ALD is introduced. Furthermore, as an example, fundamental study on AS-ALD Al_2O_3 is presented. Four Al precursors; trichloroaluminum ($AlCl_3$), dimethylaluminum chloride ($Al(CH_3)_2Cl$), trimethylaluminum ($Al(CH_3)_3$), and triethylaluminum ($Al(C_2H_5)_3$) are used for comparison, offering a comparative study of precursor ligand properties (reactivity, polarity, and geometric factors) by changing both the number of methyl (Me) and chloride (Cl) group in $AlMe_xCl_{3-x}$ (x=0, 1, and 3) and the chain length of alkyl ligands in AlC_nH_{2n+1} (n=1 and 2). Results of quantum chemical calculations of the reaction pathways show product energetics that are strongly correlated with experimental observations. The blocking properties of the four Al precursors will be compared and the results discussed based on the growth mechanism. Finally, Al_2O_3 selective pattern is successfully fabricated, which would be useful for back-end-of-line (BEOL) semiconductor process. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale.

5:00pm **AS2-WeA-15 Selective Hydration of TiO_2 and In_2O_3: A Strategy for Site-Selective Atomic Layer Deposition at Surface Defects**, *A. Martinson, E. Kamphaus, J. Jones, N. Shan,* Argonne National Laboratory, USA*; C. Luo, A. Hock,* Illinois Institute of Technology*; L. Cheng,* Argonne National Laboratory, USA*; **Ashley R. Bielinski**,* Argonne National Laboratory

While ALD is most commonly employed in uniform conformal growth, more selective precursors and processes may allow for more precise synthetic strategies including targeted reaction at subtly unique surface sites including those that lead to electronic defects. We outline a selective hydration strategy to target reaction at the step edges of rutile TiO2 and In_2O_3. We computationally and experimentally investigate the feasibility of facet- and site-selective ALD through accurate asymmetric slab models from which the free energy of adsorption at unique surface sites is leveraged to predict step selectivity. Computational evaluation of ALD precursor adsorption free energies on multiple dehydrated facets further refine the feasibility of a temperature-dependent selective hydration strategy. Initial experiments of Ga_2O_3 ALD nucleation on TiO_2 single crystals and MgO ALD on In_2O_3 broadly support the computational predictions and strategy. The strategies outlined here provide one possible route to selectively target growth at structural defects of oxide surfaces.

5:15pm **AS2-WeA-16 Self-Assembled Monolayer and “Click” Chemistry Deposition Treatments for Area-Specific Processing**, ***Chad Brick**, R. Liberatore,* Gelest, Inc*; B. Arkles,* Department of Chemistry, Temple University*; J. Goff,* Gelest, Inc

Self-assembled monolayers (SAMs) formed or modified by rapid “click” chemical reactions are receiving significant attention due to their demonstrated ability to promote or facilitate area-specific or area-selective deposition utilizing processes that occur on time scales compatible with high-throughput manufacture and cyclic deposition schemes. By precision tailoring of the chemical structure of the SAM layer, the selectivity and speed of the reactions with both the underlying substrate and subsequent deposition cycles can be enhanced in order to provide rapid, selective processes with few or no chemical byproducts. In this work we demonstrate that cyclic azasilanes and cyclic thiasilanes can rapidly bond to the surface of hydroxyl-covered substrates in the vapor phase, with saturated coverage being reached in several seconds in a manufacturing-worthy atomic layer deposition tool. The effects of processing parameters, including pulse time, temperature, substrate type, and pre-treatment on the deposition profile, as well as the subsequent reactivity of cyclic azasilanes to further modify the chemical nature of the surface are discussed, with an emphasis on rapid “click” chemical processes compatible with high throughput. It was observed that on hydroxyl (OH)-terminated surfaces such as silicon native or thermal oxide the cyclic silanes reach a saturation point in approximately five seconds under typical ALD conditions over the temperature range of 30 °C to 300 °C, as determined by water contact angle and ellipsometry. The reactivity and selectivity of cyclic azasilanes to other oxide surfaces as well as non-oxides such as copper, silicon nitride, and HF-etched silicon will be discussed, as will process to remove azasilane monolayers after deposition.

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