Area Selective ALD
Room 113-115 - Session AS-TuM

Area Selective Deposition I

Moderators: Rong Chen, Huazhong University of Science and Technology, Woo-Hee Kim, Chonbuk National University

8:00am **AS-TuM-1 Selective Area Deposition of BN using Electron Enhanced ALD**, ***Jaclyn Sprenger***, *A Cavanagh, H Sun,* University of Colorado - Boulder; *A Roshko, P Blanchard,* National Institute of Standards and Technology; *S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a line-of-sight technique and can produce selective area deposition. The electron beam activates surface sites for precursor adsorption. If a portion of the substrate surface is masked or is parallel to the electron beam, then no active sites will be generated and EE-ALD will not occur. The prospect of selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure.

EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature. GaN [1] and Si [2] have also been deposited using EE-ALD. EE-ALD uses electron stimulated desorption (ESD) to remove surface species. The ESD step in the EE-ALD of BN removes surface hydrogen. The result of ESD is a substrate surface terminated with dangling bonds. These dangling bonds are reactive and serve as sites for precursor adsorption.

Selective area deposition was investigated by growing an EE-ALD BN film on a trench structure. For a trench structure with vertical walls aligned parallel to the electron beam, there should be no electron flux and no film growth on the vertical walls. In contrast, the top and bottom of the trench will receive the full flux of the electron beam and should obtain film growth. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure (see supplemental Figure S1). BN films were observed on the top and bottom of the trench and very little BN film growth was measured on the side walls. STEM/EELS elemental mapping of B, N, Si, O and a false-color composite also showed a thick BN film on the top and bottom of the trench. Very little BN film growth was observed on the trench wall (see supplemental Figures S2).

The walls of the trench structures used in this work did not have vertical walls. In addition, the present experimental configuration did not allow for the exact alignment between the substrate surface normal and the electron gun. Even with this set-up, the effects of selective area deposition were apparent on the trench structure. The results show the promise of EE-ALD for applications such as the bottom-up-fill of trenches or vias.

[1] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, Chem. Mater. 28, 5282 (2016).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun, and S.M. George, J. Vac. Sci. Technol. A. 36, 01A118 (2018).

8:15am **AS-TuM-2 Reactive Monolayers for use in Area Selective Atomic Layer Deposition**, ***Rudy Wojtecki,*** IBM Research - Almaden; *E De Silva,* IBM Research - Albany; *N Frederick Fine Nathel,* IBM Research - Almaden; *H Shobha,* IBM Research - Albany; *N Arellano, A Friz, G Wallraff,* IBM Research - Almaden

Despite critics declaring an end to Moore's law scaling continues as technology roadmaps target feature sizes below 10nm. As we advance these roadmaps, the lithography used to define features experience increasingly significant scaling errors that include edge placement, overlay and critical dimension uniformity, which can all lead to device variation and ultimately impact device performance. Selective area atomic layer deposition (SAALD), offers the unique advantage of exploiting surface chemistry to deposit a material in a targeted area and could, in principle, eliminate a lithography step – and therefore an alignment step – that introduce these errors. This would offer not only a significant cost savings but may also relax upstream design rules and enable access to non-traditional structures (e.g. 3D patterning).

Monolayers formed from a collection of well-organized small molecules can be utilized as effective barriers to block the deposition of hundreds of ALD cycles, or in combination with repair strategies to extend selective deposition capabilities. This is an attractive strategy as it enables the implementation of well-established head group chemistry to selectively deposit the monolayer on one surface vs. another. However, in SAALD there have only been reports of monolayers where weak Van der Waals interactions are used to drive the formation of well ordered crystalline monolayers, generally long chain alkanes. When the monolayer component has a high vapor pressure this can lead to process requirements where to provide a good barrier may take as long as 48hrs. We have designed monolayer components bearing supramolecular interacting groups that aide in alignment and reduce formation time. Furthermore, functional groups can be incorporated that are subsequently reacted to produce a robust barrier that deactivate surfaces for significantly more ALD cycles in comparison to monolayers that simply exploit the weak Van der Waals interactions.

These masking materials may provide the ability to replace a lithography step in semiconductor manufacturing provided SAALD can achieve a resolution relevant to current technology nodes. Therefore, we have also evaluated these reactive monolayer blocking schemes on planar structures with critical dimensions at and below 200nm allowing us to quantify the limiting resolution of these monolayer masks. Furthermore, these schemes may provide the ability to relax design rules and enable the selective deposition on fabrication of 3D structures, an area we are currently investigating.

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8:30am **AS-TuM-3 Area-selective Atomic Layer Deposition using Si Precursor Inhibitors**, ***Mohammad Rizwan Khan,*** Incheon National University, Korea, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is envisioned to play a key role in next-generation semiconductor processing and can also provide new opportunities in the field of electronic devices. In this work, studies will be carried out to deposit the small size of Si precursor i.e., new inhibitors namely (N, N-dimethylamino) dimethylsiliane (DMADMS) and (N, N-dimethylamino) trimethylsiliane (DMATMS) on different substrates using various temperature for improving the packing quality and a highly ordered structure with uniformity and defect free, and have excellent blocking properties. A smaller size of the tail group increases the packing quality because of less steric hindrance, so less bulky tails such as DMADMS and DMATMS are more effective than branched or aryl tails such as octadecyltrichlorosilane (ODTS). Meanwhile, the other advantage of small size inhibitor is easy vaporization deposition which could be easily integrated into ALD process. The SiO_2 substrate coated with the inhibitors, yielding a hydrophobic surface with a water contact angle of about 80°-90°. For example, adsorption of DMADMS molecules with methyl (–CH_3) tail groups on an oxide substrate transforms the surface from an OH-terminated hydrophilic surface into a CH_3-terminated hydrophobic surface. The DMADMS molecules selectively adsorbed to the OH-terminated oxide areas, and AS-ALD of metal and metal oxide (Ru, Al_2O_3) was obtained on part of the surface not covered with the hydrophobic DMADMS molecules. The DMADMS adsorption on SiO_2 was investigated with techniques that include surface potential, ellipsometry, and DFT calculation. Surface reactivity of SiO_2 is decreased by adsorption of DMADMS, and thus adhesion of DMADMS coated SiO_2 is lower than DMADMS free SiO_2. The study thus provides useful information on the design of efficient ALD Si precursors with conformal, dense, and high-purity films for area selective growth.

8:45am **AS-TuM-4 *In situ* and *ex situ* Monitoring and Metrology for the Development of a Selective Deposition Process**, ***Christophe Vallee***, LTM-UGA, France; *R Gassilloud,* CEA-Leti, France; *B Pelissier, R Vallat, V Pesce, O Salicio,* Univ. Grenoble Alpes, LTM, France; *T Grehl, P Brüner,* ION-TOF GmbH, Germany; *N Posseme,* CEA-Leti, France; *P Gonon, A Bsiesy,* Univ. Grenoble Alpes, LTM, France

Different approaches are currently used for the development of Area Selective Deposition (ASD) processes such as Selective ALD using SAM, Selective ALD using block copolymer, Selective ALD using temperature and inherent selectivity, Selective ALD using spatial ALD, Selective ALD using ABC cycle, as well as Selective ALD using an etching cycle in a ALD cycle (our process). For all these approaches it is necessary to precisely control and understand the interactions and mechanisms between the precursor, the reactant and the surface. Therefore, in this paper we will show how metrology and more precisely *in situ* and *ex situ* surface characterization can play an important role for the development of an ASD process.

The ASD process used for this work is based on the idea of combining ALD and ALE (Atomic Layer Etching) and is a 3 step ASD process. Firstly, inherent selectivity or surface plasma treatment is used to start the growth on one surface versus the other. Secondly, when the growth is starting on the second surface, an etching step is added. Thirdly, after or during the etching step a surface passivation step must be used to prevent any other

growth during a given number of ALD cycles. These "super ALD cycles" can be repeated as many times as wanted to obtain the desired selective thickness [1].

Key steps for the process are that we need a precise control of the etching at the atomic scale and a control of its selectivity. Controlling the nature and density of defects induced by the etching step or the passivation steps and understanding their impact on the physical and electrical properties of the selectively deposited films are also required. Moreover, for the optimization of the process we need to precisely understand why after a given number of ALD cycles, the passivation is no more effective. Therefore, *in situ* as well as *ex situ* monitoring and metrology are bringing key advantages for these processes studies and developments. Among others, quasi *in situ* XPS [2] allows to access accurately to the chemical nature of the deposited film at each step of the process while avoiding any atmospheric unwanted oxidation. As an example, thanks to quasi *in situ* XPS, it is shown that after a passivation step on Si and TiN surfaces, more than 10 PEALD cycles are needed to start the growth of TiO_2 on Si while it is starting from the first cycle on TiN surface. Hence, with this presentation we will show how to optimize an ASD process using *in situ* ellipsometry, XPS, and OES, in addition to *ex situ* XRR and LEIS measurements.

[1] R. Vallat et al, J. Vac. Sci. Technol. A**35** (2017) 01B104

[2] B. Pelissier *et al*, Microelectronic Engineering**85** (2008) 151-155

9:00am **AS-TuM-5 Area-Selective Atomic Layer Deposition of TiN, TiO_2, and HfO_2 on Si_3N_4 in Sub-50 Nanometer Si_3N_4/Amorphous Carbon Structures***, **Eric Stevens**,* IMEC*; Y Tomczak, B Chan, E Altamirano Sanchez,* IMEC, Belgium*; G Parsons,* North Carolina State University*; A Delabie,* IMEC, Belgium

This work investigates initial growth of TiN, TiO_2, and HfO_2 thin films during thermal atomic layer deposition (ALD) onto an amorphous carbon (aC). ALD of TiN ($TiCl_4/NH_3$ 390°C), TiO_2 ($Ti(OCH_3)_4/H_2O$ 250°C), and HfO_2 ($HfCl_4/H_2O$ 300°C) on pristine aC films resulted in uninhibited thin-film growth. A H_2 plasma treatment resulted in surface reduction and passivation of aC films, with delayed film coalescence for TiN, TiO_2, and HfO_2 ALD on aC. After 200 TiN cycles on H_2 plasma-treated aC, Ti levels were below the Rutherford backscattering spectrometry detection limit (8×10^{13} at/cm^2), whereas Si_3N_4 substrates show ~6 nm of TiN growth (selectivity ~200:1). Exposing plasma-treated aC to H_2O induces nucleation for TiN ALD, consistent with favorable nucleation on hydroxyl sites. We demonstrate selectivity scaling using 45 nm aC/Si_3N_4 line/space patterns, where a 5.8 nm TiN film was deposited on Si_3N_4 with minimal particle formation on aC, with selectivity loss primarily on feature corners and edges. We conclude that improved scaling of selectivity to nanometer scale patterns can be achieved by optimizing surface loading and extent of plasma exposure, and by further understanding shape effects in nanoscale surface plasma modification.

9:15am **AS-TuM-6 Toward Area Selective ALD on Metal/Dielectric Patterns: Comparison of Cu, Co, W and Ru***, **Dara Bobb-Semple**, S Bent,* Stanford University

Device fabrication today is based on 'top-down' processes with multiple lithography and etching steps which serve as a bottleneck as well as a source of errors in device miniaturization. Area-selective atomic layer deposition (AS-ALD), which combines a surface modification technique and atomic layer deposition (ALD) in a 'bottom-up' approach to nanopatterning, shows promise in addressing these issues. A common approach in AS-ALD is to use densely-packed, self-assembled monolayers (SAMs) to modify the substrate surface and block ALD.

Incorporating this selective ALD process into fabrication schemes requires understanding how SAMs interact with different surfaces and also determining whether they can block ALD. In this work, we perform comparative investigations of the formation of octadecylphosphonic acid (ODPA) SAMs on four metal substrates: Cu, Co, W and Ru. After SAM deposition, model metal and metal oxide ALD processes were performed to assess the blocking ability of the SAM layer on each substrate. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), water contact angle (WCA) goniometry, and X-ray reflectivity were used to characterize the modified samples before and after ALD.

Solvent choice and deposition temperature were found to affect ODPA SAM formation. The most passivating SAMs of ODPA were formed on Co and Ru in t-butanol whereas on W the most passivating SAM was formed in toluene. The ODPA covered substrates showed a C/P ratio of ~20 and average WCA of 110 ± 2° which confirm SAM formation.

Testing against ALD showed that ODPA SAMs could block ALD on Cu, Co and W to varying degrees, but not on Ru. ODPA SAMs were successful in preventing growth of at least 17 nm of ZnO ALD on W, whereas only 7 nm was blocked on Co and ~5 nm on Cu. Similarly, 3-4 times more Al_2O_3 ALD was blocked using ODPA SAMs on W versus that on Cu and Co. These results suggest that a higher quality SAM is being formed on the W surface than on the other metals, which may be explained in terms of the Lewis acid character of that substrate. By implementing a sequential deposition and etch process using acetic acid as the etchant, selectivity could be extended to over 20 nm of Al_2O_3 growth on Co/SiO_2 patterns with feature sizes as small as 20 nm. These studies provide insights that are important for consideration in the development of fabrication processes which incorporate SAMs for AS-ALD. Finally, we will present developments toward SAM-free processing for achieving selective ALD on metal/dielectric patterns.

9:30am **AS-TuM-7 Advanced Cycles for Area-selective Atomic Layer Deposition***, **Adrie Mackus**,* Eindhoven University of Technology, Netherlands **INVITED**

Area-selective ALD is currently gaining momentum, motivated by its potential application in self-aligned fabrication schemes. Conventional approaches for achieving area-selective ALD were predominantly based on the local deactivation of the surface *prior* to the deposition using self-assembled monolayers or resists films, followed by standard AB-type (i.e. two-step) ALD cycles. Many of the recently developed approaches for area-selective ALD rely on adding steps *during* the ALD process to influence the selectivity of the deposition, for example in the form of ABC-type cycle,[1] or supercycle[2] processes.

In this contribution, two approaches based on advanced ALD cycles will be discussed and illustrated by recent work on area-selective ALD of SiO_2 and Ru. An ABC-type ALD cycle was developed for area-selective ALD of SiO_2, in which an inhibitor is dosed in step A that selectively adsorbs on specific surfaces and subsequently blocks the precursor adsorption in step B.[1] One of the merits of this approach is that it is compatible with the use of plasmas or ozone as the co-reactant in step C. Furthermore, the selectivity for area-selective ALD of Ru was improved by combining ALD cycles with selective etching cycles in a supercycle recipe.

The main requirements for these advanced ALD cycles will be discussed. In addition, new opportunities that are opened up by the development of these novel area-selective ALD strategies will be described.

1. A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, *ACS Nano* **11**, 9303 (2017)

2. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A*.**35**, O1B104 (2017)

Area Selective ALD
Room 113-115 - Session AS-TuA

Area Selective Deposition II

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Bonggeun Shong, Hongik University

1:30pm **AS-TuA-1 Integrated Isothermal Atomic Layer Deposition and Thermal Atomic Layer Etching: "Atomic-Level Processing" for Area-Selective Patterning of TiO_2**, ***Seung Keun Song,*** North Carolina State University; *P Lemaire,* Lam Research Corp.; *G Parsons,* North Carolina State University

Area-Selective Atomic Layer Deposition (AS-ALD) is attracting more attention from the semiconductor industry as a possible solution to alignment issues typically faced when scaling down transistor feature sizes. To address this challenge we show a new approach to AS-ALD, where self-limiting thermally-driven atomic layer etching (ALE) is chemically coupled with self-limiting thermal atomic layer deposition (ALD) to yield several nanometers of TiO_2 thin film formation on receptive SiO_2 surfaces at 170°C, with no measurable grown on adjacent areas of hydrogen-terminated silicon (100). When TiO_2 ALD using $TiCl_4$ and H_2O is done 170°C on non-oxidized hydrogen-terminated silicon, we find an incubation time of ~30 cycles is required before substantial TiO_2 nuclei appear. On SiO_2 surfaces, however, TiO_2 nucleation proceeds rapidly, allowing 10-20 Å of deposition before nucleation on Si-H. Using this inherent nucleation delay combined with a novel self-limiting thermal ALE procedure employing sequential doses of WF_6 and BCl_3, we create a new isothermal "Atomic-Level Process", where the atomic-scale chemical control of ALD is intimately coupled with that of thermal ALE to build up on a prepared surface, precise nanoscale constructs with pre-selected location and dimension. Using the integrated ALD/ALE sequence, we achieve in excess of 200 TiO_2 ALD cycles, yielding ~ 4 nm of TiO_2 on SiO_2, before visible nuclei form on Si-H, as determined by SEM, ellipsometry and TEM analysis. Process and materials analysis using in-situ QCM and ex-situ AFM and XPS further confirm our findings. To date, extending the ALD/ALE sequence to more than 500 ALD cycles leads to incomplete TiO_2 etch removal from Si-H, ascribed to changes in Si-H during prolonged exposure to deposition and etch species. This demonstrated Atomic Level Process for improved control in selective deposition offers substantial opportunities for integrated area-selective ALD, and provides a viable pathway to explore other Atomic Level Processes for parallel and wafer-scale synthesis of nanoscale and sub-nanoscale constructs.

1:45pm **AS-TuA-2 Inherent Substrate Selectivity and Nucleation Enhancement during Ru ALD using the RuO_4-Precursor and H_2-gas.**, ***Matthias Minjauw,*** Ghent university, Belgium; *H Rijckaert, I Van Driessche, C Detavernier, J Dendooven,* Ghent University, Belgium

Ruthenium is a candidate to replace copper in future sub-10 nm interconnects. At these dimensions the resistivity of Ru lines is expected to be lower compared to Cu due to the lower sensitivity to size effects.[1] In addition, it is likely that Ru interconnects won't require a diffusion barrier, and will show a better electromigration performance.[2] At feature sizes below 10 nm it will be difficult to align subsequent lithography steps, and the conformality of the deposition method is increasingly important, such that area selective atomic layer deposition (ALD) of ruthenium is of high interest.[3]

We first report inherent area selective ALD of Ru on H-terminated Si (Si-H) versus SiO_2, using the thermal RuO_4 (ToRuS™)/ H_2-gas ALD process.[4] In situ spectroscopic ellipsometry (SE) on blanket substrates shows that Ru growth initiation occurs from the first cycle on Si-H, while on SiO_2 the growth is delayed, resulting in a substrate selectivity window of ~ 70 cycles (Figure 1, a). Area selective Ru ALD was evaluated using a patterned substrate of 1-10 µm wide Si-H lines separated by 10 µm wide SiO_2 regions, and exposing it to 20 cycles of the RuO_4 / H_2-gas ALD process. Ex situ scanning electron microscopy (SEM) and cross section high resolution transmission electron microscopy (HRTEM) measurements show that a 4.5 nm Ru film could be deposited on the Si-H, with no Ru detected on the SiO_2 (Fig. 2). In vacuo X-ray photoelectron spectroscopy (XPS) experiments showed that exposure of Si-H to a single RuO_4 pulse leads to the oxidation of the Si surface, together with the deposition of RuO_2. On SiO_2 however, the surface is already oxidized, and in vacuo XPS shows that for the same exposure to RuO_4 no Ru is deposited on the surface (Fig. 3). Therefore, we propose that the mechanism behind the inherent substrate selectivity is the oxidation of the Si-H surface by RuO_4. Secondly, we report for a methodology to enhance the nucleation of the RuO_4 / H_2-gas process on oxide substrates. In vacuo XPS and in situ SE experiments show that a single exposure of SiO_2 to trimethylaluminum (TMA) makes the surface reactive towards RuO_4, which allows for Ru growth initiation from the first cycle (Fig. 1, b; Fig. 3). We propose that this is due to the combustion of surface CH_3-groups by RuO_4. As TMA is known to be reactive towards many oxide substrates, this methodology presents a way to achieve Ru metallization of virtually any surface.

[1] S. Dutta et al. *IEEE Elec. Dev. Lett.* **2017**, 38, 949.

[2] O. V. Pedreira *et al. 2017 IEEE IRPS, Monterey, CA*, 6B-2.1.

[3] P. C. Lemaire et al. *J. Chem. Phys.* **2017**, 146, 052811.

[4] M. M. Minjauw et al. *J. Mater. Chem. C*. **2015**, 3, 132.

2:00pm **AS-TuA-3 Surface Preparation and High Nucleation for Selective Deposition using Anhydrous Hydrogen Peroxide**, *D Alvarez,* ***Jeffrey Spiegelman,*** *K Andachi,* RASIRC

Creative surface protecting agents are being used in efforts to explore novel methods for Area Selective Deposition (ASD). These agents include self-assembled monolayers, patterned photoresists, plasma deposited films and others. At the same time, fast nucleation and growth of metal oxide films require creation of fully covered reactive surfaces. Surface treatment ideally will:

1. Generate high density or complete surface functionalization
2. Eliminate or minimize sub-surface oxidation
3. Increase speed and uniformity of nucleation compared to H_2O
4. Not react with organic functionality or photoresist on adjacent surfaces

Anhydrous hydrogen peroxide has been largely ignored as a potential novel reactive chemistry. There are several reasons for this. First, there is no precedent in the literature. Second, when delivered H_2O_2 is typically mixed with H_2O, which dominates the reaction. Third, this material has only recently become available in a packaged form that could integrate into selective deposition process equipment.

Hydrogen Peroxide is an attractive chemistry for area selective deposition because of both its oxidation properties and proton transfer properties. The chemistry compares favorably to Ozone (oxidation potential = 2.1V versus 1.8V for H_2O_2). It also has slightly stronger proton transfer than water (water pKa = 7.0 versus 6.5 for H_2O_2). Most critically, H_2O_2 has a very weak O-O bond, with Bond Energy = 36 kcal/mole, suggesting more energetically favorable reactivity at reduced temperatures.

Results from our work show good correlation with selective deposition requirements:

1. Nucleation surface density of hydroxyl groups (-OH) is 3-5 times greater using anhydrous hydrogen peroxide versus water on metal surfaces
2. No sub-surface oxidation on Si surfaces using anhydrous H_2O_2 for monolayer hydroxyl (-OH) surface functionalization
3. Faster nucleation and growth of Al_2O_3 on Si-H surfaces when using anhydrous H_2O_2 versus water
4. Little to no photoresist removal at temperatures up to 300°C with anhydrous H_2O_2

Other testing shows that metal oxide film quality grown using anhydrous H_2O_2 are nearly identical to those grown with ozone methods. Metal oxide films include aluminum oxide, hafnium oxide, and zirconium oxide.

The presentation will discuss details of newly discovered reactivity of anhydrous H_2O_2 on several surfaces and will outline potential ASD pathways.

2:15pm **AS-TuA-4 An Inherently Selective Atomic Layer Deposition of $MoSi_x$ -on Si (001) in Preference to Silicon Nitride and Silicon Oxide**, ***Jong Youn Choi,*** *C Ahles,* University of California San Diego; *R Hung, N Kim,* Applied Materials; *A Kummel,* University of California San Diego

As metal-oxide-semiconductor field effect transistors (MOSFETs) shrink into the <10 nm regime, it becomes a significant challenge to minimize electrical loss with a decreasing pitch especially at the contact regions. To reduce resistance in a compact geometry, selective atomic layer deposition (ALD) of transition metal disilicides is of great interest. In previous studies, selective ALD of tungsten (W) via a fluorosilane elimination process was

demonstrated using WF_6 and SiH_4 or Si_2H_6.[1,2] Selectivity was achieved by an inherently favorable reactivity of the precursors on hydrogen-terminated Si versus OH-terminated SiO_2. In this study, sub-stoichiometric $MoSi_x$ (x= 0.7–1.4) was selectively deposited by ALD on H-terminated Si (001) in preference to SiO_2 and SiN using MoF_6 and Si_2H_6 at 120°C. In-situ, X-ray Photoelectron Spectroscopy (XPS) was used to investigate the chemical composition of $MoSi_x$ ateach experimental step. To confirm selective deposition on the nanoscale, $MoSi_x$ was deposited on a Si sample patterned with SiO_2 and Si_3N_4 and cross-sectional Tunneling Electron Microscopy (TEM) was performed. It was observed that the Si-H surface termination allowed nucleation of $MoSi_x$ on Si in contrast to the inherently chemically passive (non-reactive) SiO_x and SiN surfaces. This substrate-dependent selectivity was retained for $MoSi_x$ growth of up to 10 nm with a proper N_2 purge gas to prevent any CVD components on SiO_2 and SiN. Performing additional Si_2H_6 doses after the ALD cycles allowed the incorporation of more Si into the film and increased the stoichiometry to be closer to $MoSi_2$. The $MoSi_x$ catalyzes this self-limiting CVD of Si while retaining selectivity over SiO_2 and SiN. In-situ Scanning Tunneling Microscopy (STM) showed that $MoSi_x$ ALD on Si produced an atomically flat surface with a root mean square (RMS) roughness of 2.8 Å. Post-annealing in ultra-high vacuum at 500°C for 3 minutes further decreased the RMS roughness to 1.7 Å. A depth profiling XPS study revealed that the bulk of the $MoSi_x$ film is close to stoichiometric $MoSi_2$ with <10% oxygen and fluorine. The TEM imaging shows that the selectivity is retained on the nanoscale and that $MoSi_x$ can be selectively deposited on Si without substrate consumption. This is enabled by just taking advantage of the selective ALD of substiochiometric $MoSi_x$ combined with the ability of the substiochiometric $MoSi_x$ films to selectivity induce self-limiting Si deposition from Si_2H_6.

1. Ph. Gouy-Pailler *et al.*, Thin Solid Films, **241**, 374 (1994)

2. B. Kalanyan *et al.*, Chem. Mater., **28**, 117-126 (2016).

2:30pm **AS-TuA-5 Investigating the Difference in Nucleation during Si-based ALD on Different Surfaces (Si, SiC, SiO_2 and SiN_x) for Future Area-Selective Deposition (AS-ALD)**, ***Ekaterina A. Filatova,*** Tyndall National Institute, University College Cork, Ireland*; A Mameli, A Mackus,* Eindhoven University of Technology, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands*; W Kessels,* Eindhoven University of Technology, Netherlands*; D Hausmann,* Lam Research Corp.*; S Elliott,* Schrödinger, Inc., Ireland

Area-selective atomic layer deposition (AS-ALD) allows nanostructures of arbitrary composition and lateral shape to be built with atomic precision on pre-selected substrate locations. Most current approaches for AS-ALD are based on local inhibition (e.g. with self-assembled monolayers) or activation. However, for some applications of AS-ALD (e.g. in self-aligned fabrication) it is relevant to be able to exploit differences in chemical behavior of a pre-patterned substrate. For this reason, investigating inherent differences in nucleation on diverse substrates is of crucial importance for developing future AS-ALD processes. In this paper we are focussing on substrates of silicon and silicon-based dielectric materials (SiC, SiO_2 and SiN_x) used in electronics.

In order to investigate the possibility of area-selective deposition of Si-based materials using aminosilane precursors, nucleation on four different Si-based surfaces (Si:H, SiC:H, SiO_2:OH and Si_3N_4:NH_2/NH) was analyzed. First, we investigated the difference in precursor adsorption on these surfaces during the exposure of di(isopropylamino)silane (DIPAS), di(sec-butylamino)silane (DSBAS) and bis(t-butylamino)silane (BTBAS) precursors by calculating their adsorption energies using ab-initio modelling. From density functional theory (DFT) calculations, we found that DSBAS is thermodynamically favorable to react with Si_3N_4 and SiO_2, but not with SiC and Si at 0K. To experimentally corroborate these results, SiN_x was deposited using Plasma-Enhanced ALD from DSBAS precursor and N_2 plasma on three different surfaces (H_2 plasma-exposed SiC, HF-last c-Si and c-Si with native SiO_2). In-situ spectroscopic ellipsometry (SE) measurements were performed after every half-cycle to analyze the DSBAS adsorption reaction on these surfaces. During the first DSBAS dosing cycle on the SiO_2 surface a change in the SE signal was observed, suggesting initial DSBAS adsorption, while no changes were observed on the Si and SiC surfaces. The selective adsorption of DSBAS on SiO_2 is in agreement with the DFT predictions. The subsequent N_2 plasma half-cycle modifies the non-growth surface into SiN_x, after which the selectivity is lost. These results illustrate that it is generally difficult to achieve area-selective ALD for nitrides, because of the nitridation of all the exposed substrate surfaces during the plasma step.

We conclude, that during ALD on Si-based substrate materials DSBAS reacts selectively with SiO_2 and SiN_x surfaces but not with Si and SiC surfaces. Our results highlight the role of DFT calculations in predicting possible routes towards AS-ALD process development.

2:45pm **AS-TuA-6 Strategies for Area Selective Atomic Layer Deposition and Applications in Catalysis**, ***Rong Chen****, K Cao, X Liu, J Cai, B Shan, J Zhang,* Huazhong University of Science and Technology, China **INVITED**

Atomic layer deposition (ALD) is a mainstay technology for the semiconductor industry since it allows deposition of nanometer-thin layers of desired materials onto a substrate in a very controlled and uniform manner. Recently, ALD has been adapted to design and synthesize composite catalysts that allow them to promote multiple chemical reactions. In fabrication of composite catalysts, the selective approaches of ALD are of great importance to exert spatial control of deposition to fabricate three dimensional nanostructures.

In this talk, strategies for selective ALD and enabled nanostructures for catalytic applications will be discussed. Selective ALD allows directional and precise tailoring of the structural size, composition, interfaces, and active sites, that is of great importance for catalysis applications. Two major types of selective ALD approaches are introduced, template selective method via surface modification of self-assembled monolayers (SAMs) and reverse SAMs passivation, as well as inherently selective deposition. With these methods, core shell nanoparticles, oxide overcoating structures ranging from porous coating to ordered structures, and oxide surrounding structures could be fabricated controllably. Theoretical simulations, spectroscopic and microscopic analysis, and catalytic performance are carried out to verify the results. These strategies of selective ALD demonstrate unique advantages to design and fabricate highly stable and active catalysts on the atomic scale, providing unique opportunities to understand the structure–property relationship of catalysis.

Area Selective ALD
Room Premier Ballroom - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Use of Low Energy Ion Scattering for the Analysis of Area Selective ALD Processes, ***Thomas Grehl,*** *P Brüner,* ION-TOF GmbH, Germany*; C Vallee,* LTM-UGA, France*; R Gassilloud,* U Grenoble Alpes, CNRS, LTM*; V Pesce, A Bsiesy, B Pelissier,* Univ. Grenoble Alpes, LTM, France

Low energy ion scattering (LEIS) is a surface analytical technique that enables the characterization of the outermost atomic layer of a sample. The sample is bombarded with noble gas ions with kinetic energies of a few keV, and the energy spectrum of the backscattered ions is recorded. Ions scattered by different atom species in the first atomic layer give rise to distinct elemental peaks in the energy spectrum. As the result of the scattering process is independent of the chemical environment of the target atom, the peak intensities are directly proportional to the surface coverage of the respective element. The elemental composition of the surface can thus be determined in a quantitative way.

In addition to surface scattering events, noble gas ions scattered in deeper atomic layers undergo material-dependent energy losses proportional to their penetration depth. These processes lead to additional sub-surface features in the energy spectra, which can be evaluated to obtain layer thickness values and the depth distribution of elements in the first few nm of a sample.

The extreme surface sensitivity of just a single monolayer is a unique property of LEIS that is not available with other surface analytical techniques like XPS or SIMS, which always integrate over several monolayers. This makes LEIS an ideal tool to study layer growth in ALD processes. The monolayer sensitivity is especially useful to analyze the early stages of film growth, with questions about topics like surface coverage, layer closure, nucleation delay, growth mode, growth rate, or the presence of impurities.

Additional complexities arise in the field of area selective deposition (ASD). A higher number of process steps are involved, and often additional reactants lead to more complex chemical interactions. Growth areas and non-growth areas are present simultaneously, and surface analytical tools become increasingly important to develop, understand, and improve deposition processes.

One example of an ASD process, developed at LTM, includes an atomic layer etching (ALE) step once nucleation sets in on the non-growth area. The area is then passivated to restore its non-growth properties, and deposition is resumed. This cycle is repeated until the desired film thickness is obtained on the growth area. In this study, we apply LEIS to a series of model samples of thin ALD TiO_2 layers, created to improve understanding of this ASD process. The passivation step and the precise point where nucleation re-starts on the passivated area are of special interest. Moreover, the influence of the fluorine-based plasma etching on the deposited TiO_2 layers is investigated.

AS-TuP-2 Area-Selective Atomic Layer Deposition of Zinc Sulfide Based on Inherent Selectivity*, Chao Zhang*, *Z Han, M Vehkamaki, M Leskelä, M Ritala,* University of Helsinki, Finland

The need for simplifying and improving complex electronic device fabrication has motivated the research on area-selective atomic layer deposition (ALD). Area-selective ALD is a bottom-up approach enabling deposition of thin films only on the desired surface areas, thereby accomplishing film patterning more easily as compared with conventional lithography .[1]

It is well known that ALD process involves chemical reactions between precursors and reactive sites existing on substrate surfaces. So, in principle area-selective ALD can be achieved by surface modification including surface passivation and activation. Surface passivation means that reactive sites on the substrate surface are blocked by passivation layers, thus losing their reactivity with ALD precursors. Area-selective ALD by surface passivation has already been studied for years, focusing on using self-assembled monolayers (SAMs) or polymers as resist layers to prevent the film growth.[2]On the contrary, surface activation provides an opposite way to attain selective film growth by patterning of seed layers that can promote ALD film growth catalytically. For example, Färm et al. proved an easy way that used micro contact printed RuO_x films as a seed layer for catalyzing ruthenium ALD process .[3]

Here, a new approach based on inherent selectivity of an ALD process is presented for area-selective ALD. It is found that ALD of ZnS, using elemental zinc and sulfur as precursors at a deposition temperature of 500°C, takes place on Au surfaces but not on Si surfaces with about 2 nm native SiO_2 on top. As a reason for this selectivity, it is suggested that sulfur adsorbs much stronger on Au than on SiO_2. The continuous ZnS growth even after the Au surface is completely covered with ZnS can be similarly explained in terms of strong adsorption of sulfur on ZnS. Alternatively, the selectivity could also arise from Zn alloying with Au, this alloy then reacting with the subsequent sulfur pulse. Patterned Au structures used in our experiment consist of three different size dots (500, 250, 50 µm), prepared by electron beam evaporation (EBE) with a shadow mask. After the deposition of ZnS on this patterned surfaces, ZnS films were detected only on Au dots as confirmed by EDX measurements.

References

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[2] A. Mackus, A. Bol, and W. Kessels, Nanoscale **6,** 10941 (2014).

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AS-TuP-3 Selective Etching of Native Silicon Oxide in Preference to Silicon and Silicon Oxide, *C Ahles,* ***Jong Youn Choi,*** *A Kummel,* University of California San Diego

The selective removal of native SiO_x in the presence of SiO_2 would be of great importance to the semiconductor industry given the ubiquity of these two materials in electronic devices. Methods of native SiO_x removal have been well studied and typically rely upon HF chemistry. Aqueous HF treatment suffers from an inevitable air exposure of the Si sample and is not selective for native SiO_x versus bulk SiO_2. The Siconi™ process utilizes a NF_3/NH_3 plasma to remove native SiO_x leaving behind a $(NH_4)_2SiF_6$ salt as the etch product. This salt is then removed in a subsequent anneal. While this process is known to work well for removing native SiO_x on Si, the selectivity of this process versus thermal SiO_2 has not been studied. In this study, the etch rates of Si and SiO_2 subjected to a $NF_3/NH_3/Ar$ plasma were examined. Under the optimized conditions of $NF_3:NH_3:Ar$ = 1:10:1.5 at 45°C, 190 mTorr and 100 W no etching of Si is observed with negligible or no etching of SiO_2.

The etch rates of Si and SiO_2 subjected to a $NF_3/NH_3/Ar$ plasma were measured in-situ using a pair of quartz crystal microbalances (QCMs). It was found that the etch rate of Si shows a strong dependence on the temperature, with the Si etching at a rate of 25 nm/min at 50°C while no etching of Si is observed at 40°C. At 45°C, it was found that the native SiO_x on Si is rapidly etched under these conditions, after which there is only deposition (presumably of NH_4F and NH_4FHF salts). X-Ray Photoelectron Spectroscopy (XPS) measurements show that after the dry clean the Si surface has a N:F ratio of 1:3, consistent with $(NH_4)_2SiF_6$ formation. A subsequent anneal at 120°C removes the salt and leaves a very clean Si surface (1% O, 6% C, 1% F and 92% Si^0). Atomic Force Microscopy (AFM) shows that the Si surface has a root mean square (RMS) roughness of 1.1 Å. For comparison, the RMS roughness of a degreased Si sample (containing native SiO_x) which was not subjected to the dry clean was found to be 2.2 Å. This is consistent with no etching of the underlying Si, as etching would be expected to roughen the surface. XPS analysis of SiO_2 after the dry clean showed that on SiO_2 the N:F ratio was closer to 1:2, suggesting the presence of NH_4FHF instead of $(NH_4)_2SiF_6$ (the expected etch product of SiO_2). Annealing at 120°C removed most of the NH_4FHF salt, leaving behind only 4% F and 2% N. AFM measurements show that the degreased SiO_2 has an RMS roughness of 4.3 Å while after the dry clean the RMS roughness is very similar (3.8 Å), consistent with no etching of SiO_2. The reason for this selectivity may be due to the presence of more strained Si-O bonds or undercoordinated Si atoms in native SiO_x than in SiO_2.

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