Area Selective ALD
Room Grand Ballroom H-K - Session AS1-TuM

Area-Selective ALD Techniques

Moderator: Adrie Mackus, Eindhoven University, Netherlands

10:45am **AS1-TuM-12 Overview of Wet And Dry Selective Processes Driven by Area Activation or Deactivation Down to Below 20nm Critical Dimensions***, **Silvia Armini**,* IMEC, Belgium **INVITED**

Area selective deposition (ASD) is proposed as a method for preferentially depositing a material on a specific area on the surface while the remainder is left uncoated, providing spatial control over a deposited thin film. In the context of downscaling microelectronics components below 1x nm of critical dimension, ASD by Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or Electroless Deposition (ELD) offers the potential to relax downstream processing steps by enabling self-aligned patterning processes, such as self-aligned vias and tone reversal, or bottom-up metallization schemes, such as supervia or via prefill. Due to the limitations of inherent ALD selectivity, we focus our work on material surface functionalization by selective grafting thin organic films both in ALD activation and passivation mode or by plasma exposure.

For ASD ALD processes which relies on delayed nucleation on a non-growth area, defectivity and the lack of a wide portfolio of application-relevant materials are two of the main concerns for the adoption of this technology in nanofabrication. Among the strategies addressing the defectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

In this study, we review our current understanding of the relationship between structure and properties of the inhibiting/activating materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films deposited from the liquid and vapor phase on 300mm wafers or by plasmas will be analyzed and wet depassivation processes with be investigated in the attempt of removing the defects formed on top of the inhibition films.

In an attempt to understand the interaction between the ALD conditions (i.e. temperature, coreactants...) to the decomposition and modification of the organic films, in-situ XPS is exploited such as high sensitivity characterization techniques such as Secondary Ion Mass Spectrometry (SIMS).

Finally, the selectivity of the passivation and subsequent ASD process will be evaluated as a function of the patterned pitch size down to 16nm half-pitch structures. We aim at building some understanding about the relationship between the changes in surface composition due to the patterning, pitch variation and/or due to diffusion (in case of mobile species such as metals) and the ASD performance.

11:15am **AS1-TuM-14 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Cobalt Metal Films at Room Temperature***, **Zach Sobell,** A Cavanagh, S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is possible at room temperature by using electrons to stimulate the desorption of surface species. The electron stimulated desorption (ESD) process opens up free surface sites that enable the adsorption of reactants. ALD can be achieved by sequential application of electron and reactant exposures. A variety of materials have been deposited using EE-ALD at room temperature including GaN, Si and BN. Because EE-ALD is dependent on the electron flux, EE-ALD films are deposited only on surface areas illuminated by the electron beam.

In this study, Co EE-ALD was performed using sequential, self-limiting cobalt tricarbonyl nitrosyl [$Co(CO)_3NO$ (CTN)] and low energy electrons exposures at room temperature. The electron energies were varied from 75 to 175 eV. In the Co EE-ALD process, the CTN molecules first adsorb on the substrate. The electrons then induce ESD of the carbonyl (CO) and nitrosyl (NO) ligands from the adsorbed CTN. The ESD produces reactive surface sites. Subsequent CTN exposures react with the reactive surface sites and add Co to the substrate. The consumption of the reactive surface sites produces self-limiting Co EE-ALD.

In situ ellipsometry measurements observed a maximum growth rate of 0.5 Å per cycle at an electron energy of 125 eV. The in situ ellipsometry measurements also could monitor the CTN adsorption and the desorption of CO and NO ligands (see supplemental Figure 1). Quadrupole mass spectrometer (QMS) measurements confirmed the desorption of CO and NO during electron exposures. The spatial profile of the Co EE-ALD film resulting from the finite surface area illuminated by electrons was mapped by ex situ ellipsometry. This spatial profile was used to calculate an ESD cross section of $\sigma = 1x10^{-16}$ cm^2. This ESD cross section is close to the electron dissociation cross section for CTN observed in the gas phase.

There are many applications for EE-ALD because the ESD process is topographically selective. This area selectivity comes from the directionality of the electron flux. Surfaces normal to the incident electrons receive the full electron flux, whereas surfaces parallel to the incident electron path receive no electron flux. EE-ALD should be useful for the bottom-up fill of high aspect ratio structures like trenches and vias. EE-ALD may also be important for depositing ALD films on thermally-sensitive substrates. In addition, EE-ALD could be valuable for enhancing the nucleation of ALD films by creating reactive surface species on the initial substrate.

11:30am **AS1-TuM-15 Area Selective Atomic Layer Deposition on Molecular Design***, **Akihiro Nishida**, T Yoshino, N Okada, A Yamashita,* ADEKA Corporation, Japan

Area selective atomic layer deposition (AS-ALD) is promising as a self-aligned fabrication method and has become more important in recent years. Several types of AS-ALD precursors and processes have been developed all over the world so far. We recognize the importance of AS-ALD technology as well and have studied it for many years. However, it is challenging to achieve a high selectivity and hence investigation of molecule design and surface chemistry are essential factors to clarify the mechanism of selective deposition and film growth.

In this study, we have carried out the investigation on the effect of surface selectivity using several types of Co ALD precursors, and found that selectivity was affected by high steric hindrance structure, chemical surface characteristics and so on. Based on the results, new Co ALD precursors having a good selectivity have been developed. As an example, Bis(N-tert-butyl-N'-1-methyl-2-dimethylaminoethyl-acetamidinato)cobalt (II) [CBPA-1] has high selectivity and is liquid at room temperature. CBPA-1 showed a very clean TG curve without decomposition and residue at 10 Torr. Additionally, thermal ALD of thin Co metal film was demonstrated using CBPA-1 and hydrogen as the co-reactant on Ru and SiO_2 substrates, and succeeded in making shiny metallic Co films at 150-300 °C only on the Ru substrate. Regarding film quality, X-ray photoelectron spectroscopy (XPS) shows that high purity Co film was deposited. As a comparison, we also carried out thermal ALD using reference precursor Bis(N, N'-di-tert-butyl-acetamidinato)cobalt (II). However, Co was detected on both Ru and SiO_2 substrates over 275 °C by X-ray fluorescence (XRF) measurement. As a conclusion, CBPA-1 is better suited for Co AS-ALD process compared to conventional precursors such as dicobalt hexacarbonyl tert-butylacetylene (CCTBA) and Co amidinates complex. On top of that, a reducing method of isolated particles growth on SiO_2 substrate by using aminosilane was found out so it will be reported likewise.

11:45am **AS1-TuM-16 From Surface Dependence in Atomic Layer Deposition to Area-Selective Deposition of TiN in Nanoscale Patterns***, **Annelies Delabie**,* IMEC, Belgium*; D Carbajal,* UNAM*; J Soethoudt, B Chan, E Altamirano Sanchez, B Meynaerts, J Clerix, S Van Elshocht,* IMEC, Belgium

Area-selective deposition (ASD) holds potential for nano-electronic device manufacturing for bottom-up deposition in small trenches or holes, or to create nanoscale structures with great precision by self-alignment. Under certain surface and deposition conditions, material can grow selectively on a predefined pattern, while the rest of the surface remains unaffected. Nevertheless, ASD by atomic layer deposition (ALD) has been studied only for a limited number of materials. In addition, defectivity in the non-growth area is a challenge as inhibition in ALD is associated with island growth [1]. Insight into the surface dependence and growth mechanisms is needed to design highly selective ASD processes for relevant materials for nano-electronic devices.

First, we compare the inherent selectivity for a range of thermal ALD processes for oxides, nitrides and metals by investigating the surface dependence on blanket substrates. OH-terminated SiO_2 is the growth surface as all ALD processes considered here show linear growth on this surface, while CH_3-terminated SiO_2 is the non-growth surface. Both precursor and co-reagent affect selectivity (figure 1a). The selectivity for H_2O based ALD depends on the precursor in the order $TiCl_4$ > $HfCl_4$ > $Al(CH_3)_3$. The selectivity is higher for $TiCl_4/NH_3$ ALD than for $TiCl_4/H_2O$ ALD in spite of the higher deposition temperature.

In view of the high inherent selectivity of $TiCl_4$/NH_3 ALD, we investigate TiN ASD in nanoscale patterns consisting of Si_3N_4 spaces and amorphous carbon (aC) lines with a critical dimension (CD) of 45nm. This material system is relevant for a tone inversion application of ASD for line-space patterning [2]. A H_2 plasma pretreatment enables ASD by passivating the aC surface by formation of methyl groups [2,3]. The selectivity for Si_3N_4 versus aC is 0.94 for 6.4 nm TiN, even higher than for OH- versus CH_3-terminated SiO_2 (blankets). The selectivity is maintained for ALD temperatures between 250 and 390° C. However, in nanoscale patterns, the selectivity is affected by impurities due to patterning. By considering surface cleans before ASD, we demonstrate ASD of 7.5nm TiN on the 45nm CD line-space patterns, with little to no TiN detected on the aC top surface and sidewalls by transmission electron microscopy (Figure 1b).

[1] J. M. Mackus et al, Chem. Mater. 2019, 31, 2

[2] E. Stevens et al, Chem. Mater. 2018, 30, 3223

[3] I. Zyulkov et al, ACS Appl. Mater. Interfaces 2017, 9, 31031

Area Selective ALD
Room Grand Ballroom H-K - Session AS1-TuA
Area-Selective ALD by Area-Deactivation

Moderators: Rong Chen, Huazhong University of Science and Technology, Jessica Kachian, Intel Corp.

1:30pm **AS1-TuA-1 Elucidating Mechanisms of Selective ALD of Al_2O_3 by a Comparative Study of Precursors***, **Il-Kwon Oh**, T Liu,* Stanford University*; T Sandoval,* Technical University Federico Santa Maria*; R Tonner,* Philipps-Universität Marburg, Germany*; S Bent,* Stanford University

Area-selective atomic layer deposition (AS-ALD) 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.[1] 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, we study the growth mechanism of $Al_2O_3$with four Al precursors; trichloroaluminum (TCA), dimethylaluminum chloride (DMACl), trimethylaluminum (TMA), and triethylaluminum (TEA). They offer 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. For example, with increasing number of Cl ligands, the growth rate is found experimentally to increase at low temperature, consistent with a large initial adsorption energy of TCA on Si .Interestingly, although they have similar geometrical factors, the precursors exhibit different ALD growth rates (0.75, 1.0, and 1.2 Å/cycle for for TCA, DMACl, and TMA respectively) corresponding to the calculated trend in activation energies as the Cl number increases. AS-ALD of Al_2O_3 using octadecyltrichlorosilane SAMs as an inhibitor is also investigated; the blocking properties of the four Al precursors will be compared and the results discussed based on the growth mechanism. By pursuing first principles design of selective ALD processes, this work may enable new methods for additive nanoscale patterning.

(1) Bobb-Semple, D. et. al., *Chem. Mater.***2019**, acs.chemmater.8b04926. https://doi.org/10.1021/acs.chemmater.8b04926.

1:45pm **AS1-TuA-2 Area-Selective Atomic Layer Deposition using Dodecanethiols: Comparison of Monolayer versus Multilayer***, **Tzu-Ling Liu**,* Stanford University*; K Nardi, N Draeger, D Hausmann,* Lam Research Corp.*; S Bent,* Stanford University

As the size of transistors continues downward scaling, more difficulties are introduced into traditional top-down semiconductor fabrication processes, such as edge placement errors and two-dimensional overlay control. In addition, the number of processing steps and cost are becoming significant. To overcome these challenges, it is necessary to develop new techniques, and selective deposition is one promising solution to reduce patterning errors and process complexity. Atomic layer deposition (ALD) is considered to be well suited for selective deposition because of its self-limiting reactions between precursors and specific functional groups at the substrate surface. By manipulating the surface functional groups with self-assembled monolayers (SAMs), area-selective ALD has been successfully demonstrated on technologically-important metal/dielectric (Cu/SiO_2) patterns. In recent years, using alkanethiols as the inhibition layer has received much attention because they can be deposited onto metal surface via a vapor-phase approach that can be readily incorporated into industrial semiconductor fabrication processes.

Despite the apparent simplicity of the alkanethiolate SAM system for AS-ALD, recent studies have shown that either a monolayer or multilayers of the thiols can form on Cu depending on the preparation details, including a dependence on the oxidation state of the Cu surface. However, the effect of having multilayer versus monolayer thiols on the blocking ability in AS-ALD of metal oxides has not been reported.

In this work, we compare the ALD blocking ability of multilayer and monolayer dodecanethiols (DDT) deposited from the vapor phase. The results show that monolayer DDT films are better than multilayer DDT films at inhibiting Al_2O_3 ALD. In contrast, the multilayer DDT films show better blocking performance against ZnO ALD. The influence of monolayer and multilayer DDT on area selective deposition of ALD films onto Cu/SiO_2 patterns is also studied. On the multilayer DDT-coated Cu/SiO_2 patterns, we show that there is a nucleation delay for ZnO ALD on SiO_2 near its interface with Cu, resulting in a thinner ZnO film at the edge of the SiO_2 region, an effect which is pitch dependent. The possible mechanism underlying this phenomenon will be discussed.

2:00pm **AS1-TuA-3 Mechanism for Breakdown in Selectivity During Area-Selective Atomic Layer Deposition of ZrO_2 on a SiO_2 Surface Functionalized with a Blocking Layer***, **Wanxing Xu**,* Colorado School of Mines*; P Lemaire, K Sharma, D Hausmann,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

The conventional lithography is becoming increasingly challenging due to continued downscaling of modern semiconductor devices. Area-selective deposition of dielectrics and metals can simplify patterning for next-generation devices. Atomic layer deposition (ALD) has emerged as a very promising technique for achieving selective deposition because film growth during ALD is highly sensitive to the surface functionalization of the underlying substrate. In this study, we focus on the area-selective ALD of ZrO_2 on metals while inhibiting growth on SiO_2 by terminating the surface with fluorocarbon or hydrocarbon ligands.

The starting SiO_2 surface was functionalized with the inhibitor molecules: nonafluorohexyldimethyl(dimethylamino)silane (NHDDAS) , *n*-octyldimethyl(dimethylamino)silane (ODDAS), or *n*-octadecyltrichlorosilane (ODTS). The aminosilanes were attached to –OH-terminated SiO_2 either through the vapor phase or in solution, while ODTS was attached to surface through the solution phase. The functionalized SiO_2 surfaces were characterized by Fourier transform infrared (FTIR) spectroscopy, ellipsometry, and water contact angle measurements. We show that aminosilane and chlorosilane precursors react with almost all of the surface –SiOH groups forming ºSi–O–Si–R bonds on the surface (see Figure 1). This surface functionalization is stable over the temperature range of 200–300 °C.

ZrO_2 was grown by ALD on the passivated SiO_2 surfaces using either tetrakis(ethylmethylamino)zirconium(IV) (TEMAZ) $[Zr(NCH_3C_2H_5)_4]$ or zirconium(IV) tert-butoxide (ZTB) $[Zr(OC(CH_3)_3)_4]$, and H_2O over a temperature of 200–250 °C. While no ZrO_2 growth was detected during the initial few cycles, *in situ* four–wavelength ellipsometry showed that growth inhibition breaks down after an increased number of cycles. We recorded the corresponding surface reactions during ZrO_2 ALD using *in situ* attenuated total reflection FTIR spectroscopy, which allows us to identify the surface reaction sites and adsorbed surface species. Surprisingly, after repeated exposure of the functionalized SiO_2 surface to TEMAZ and ZTB, these precursors reacted with Si–O–Si bonds in the absence of surface –SiOH groups (see Figure 2). This suggests that while ALD of ZrO_2 may proceed through reaction with surface –OH groups, other reactions with a higher activation energy barrier become important as these surface reactive sites are removed through surface functionalization. These results highlight the importance of steric blocking of the substrate surface as an additional requirement for growth inhibition during ALD.

2:15pm **AS1-TuA-4 Area Selective Chemical Vapor Deposition of Co from the Co (CO) Precursor: Use of Ammonia to Afford Dielectric-Dielectric Selectivity***, **Zhejun Zhang**, S Liu, G Girolami, J Abelson,* University of Illinois at Urbana-Champaign

We previously reported the area selective chemical vapor deposition of MoC_xN_y thin films on metal substrates using $Mo(CO)_6$ precursor with a coflow of NH_3 inhibitor: at temperatures of 150-210 °C, film grows readily on metal or metal nitride surfaces but nucleation and growth are suppressed on all oxide surfaces. This was attributed to the site-blocking of hydroxyl groups or a reduction in the acidity of the surface by NH_3.

Here, we demonstrate chemical vapor deposition of cobalt thin films that is *area-selective between oxide surfaces* using $Co_2(CO)_8$ precursor with a coflow of NH_3 inhibitor at 70 °C: growth is suppressed on acidic oxides such

as SiO_2 and WO_3 during experiments lasting up to 60 minutes, but proceeds unimpeded at rate of 0.6 nm/min on basic oxides such as Al_2O_3, HfO_2 and MgO. Selectivity of > 99% between SiO_2 and Al_2O_3 can be obtained. In the absence of ammonia, nucleation occurs readily on all oxide substrates but the area density of nuclei, and consequently the film smoothness, are better on Al_2O_3 than on SiO_2. Cobalt films grown with and without ammonia have a resistivity ranging from 15–25 µΩ·cm and 11–20 µΩ·cm, respectively. Surprisingly, in the presence of a very small partial pressure of NH_3, growth can proceed on SiO_2 and the area density of nuclei is *increased*. To account for these observations, we propose that ammonia reduces the surface diffusion of adsorbed precursor. Under this hypothesis, for small NH_3 pressure, adsorbates may react to form new nuclei instead of being transported to, and incorporated into, existing nuclei; but at high NH_3 pressure, adsorbate-adsorbate interaction may be suppressed, such that the rate of desorption outpaces that of nucleation.

2:30pm **AS1-TuA-5 Area-Selective ALD of Silicon Oxide using Inhibitors in Four-step Cycles for Metal/Dielectric Selectivity**,
***Marc Merkx**, R Jongen,* Eindhoven University of Technology, Netherlands*; A Mameli,* TNO/Holst Center, Netherlands*; D Hausmann,* Lam Research Corp.*; E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

The fabrication of nanoelectronics at sub-5 nm dimensions using conventional top-down fabrication schemes is becoming more and more difficult due to the increasingly straining requirements in alignment. Area-selective ALD allows for deposition of material in a self-aligned fashion and thereby enables more reliable device fabrication. In our previous work, area-selective ALD of ~1 nm SiO_2 was demonstrated using three-step (ABC) ALD cycles consisting of acetylacetone (Hacac) inhibitor (A), $H_2Si[N(C_2H_5)_2]_2$ precursor (B), and an O_2 plasma co-reactant (C) doses.[1] In this contribution, the reaction mechanisms involved in cyclewise removal and reapplication of inhibitor molecules will be described. Based on the acquired insights, new opportunities and challenges for this approach will be discussed.

The reapplication of the inhibitor allows for the use of ozone or plasmas as the co-reactant, which is one of the merits of the approach. However, using in situ infrared spectroscopy it was found that the Hacac molecules are not completely removed during the O_2 plasma exposure. Remaining Hacac fragments hinder the Hacac adsorption in the subsequent ALD cycle, and thereby decrease the selectivity. The challenge of reapplying the inhibitor molecules every cycle is therefore to ensure that the non-growth area is returned to its original state before the next inhibitor dose. In order to completely remove all Hacac species, a four-step (ABDC) ALD cycle was developed which employs a H_2 plasma step prior to the O_2 plasma exposure. The added H_2 plasma, significantly improves the selectivity, such that ~2.5 nm SiO_2 can be deposited selectively in the presence of an Al_2O_3 non-growth area.

In general it is challenging to use an O_2 plasma on structures with metal areas, due to potential oxidation of the metal during the plasma exposure which reduces the conductivity. However, the H_2 plasma in the ABDC cycle was found to largely remove the precursor ligands, and therefore only a very mild O_2 plasma exposure is required for SiO_2 deposition. In this way, area-selective ALD was achieved relative to Co as the non-growth area without significant damage to the Co substrate. The application possibilities of this ABDC-type ALD process for reliable interconnect fabrication (i.e. self-aligned VIA) will be discussed.

[1] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, A.J.M. Mackus, ACS Nano **11**, 9303-9311 (2017)

2:45pm **AS1-TuA-6 Selective Area Growth of Deactivating Polymers**,
***Rudy Wojtecki**,* IBM Research - Almaden*; T Pattison,* University of Melbourne, Australia*; A Hess, N Arellano, A Friz,* IBM Research - Almaden

As the semiconductor community continues scaling, area selective atomic layer deposition (ASD) offers the potential to relax down-stream processing steps by enabling self-aligned strategies (e.g. self-aligned via). ASD can be achieved under a variety of conditions and, with the use of organic inhibiting materials, exhibit high levels of selectivity during depositions. However, the organic materials exploited are generally relegated to small molecules and may require multiple cycles of etch-back processes followed by renewal of the surface protection coating. Recent work has shown that a variety of polymeric materials offer the potential to broaden the number and film compositions that can be selectively deposited. However, an attractive ASD approach requires the directed grafting of polymers to a surface using selective adhesion groups, for instance. Inhibiting polymers could be functionalized with metal binding ligands and the resulting polymer brushes retain their inhibiting properties on blanket films. On patterned surfaces though, brushes exhibit poor selectivity, adhering to both metal and dielectric surfaces and resulting in high defectivity after a subsequent atomic layer deposited (ALD) film (polymer particles were observed on both a metal and dielectric). An alternative approach is a grafting from strategy where a low molecular weight monomer, containing a diphosphonic acid binding group, enables area selective grafting on a prepatterned surface containing copper lines and silicon spaces. Subsequent treatment of these surfaces with a catalyst and introduction of a norbornene monomer in the vapor phase allows the area selective growth of polynorbornene (PNB) producing films with thicknesses between 10-100nm. The surface grown PNB films shows excellent inhibitory properties against the ALD deposition of metal oxides, TiO_2 and ZnO, where only trace metal concentrations are observed on the polymer surfaces even after a long number of ALD cycles. This area selective surface grown polymer strategy offers the potential to address several challenges in ASD such as: (i) lateral overgrowth of an ALD film once film thickness exceeds that of the inhibiting material. A polymer strategy offers the potential to control the polymer film thickness and thus the desired ALD film thickness (ii) On patterned surfaces line edges and corners are sites for significant defectivity in ASD. The surface growth of a polymer readily covers these corners and edges to ensure these features are protected during the ALD process.

3:00pm **AS1-TuA-7 Area-Selective ALD of ZnO Films Patterned by Electrohydrodynamic Jet Printing of Polymers with Sub-Micron Resolution**,
***Tae Cho**, N Farjam, C Pannier, C Huber, O Trejo, C Allemang, E Kazyak, R Peterson, K Barton, N Dasgupta,* University of Michigan

An increasing demand for customization in manufacturing of integrated nanosystems has motivated the development of printable electronics that can be adapted to the unique requirements of an end-user. The current state-of-the-art in nanofabrication of functional devices involves multiple lithographic patterning steps, combined with thin-film deposition and top-down etching processes. While this has led to tremendous advances in spatial resolution and process reliability, lithographic processes are inherently parallel processes, and not easily customizable. In contrast, additive manufacturing processes enable rapid prototyping of 3-D structures that can be easily tuned, and multiple layers of dissimilar materials can be integrated in a bottom-up manner. Therefore, combining a 3-D printing technology with area-selective ALD could enable a new paradigm in customizable nanomanufacturing.

Area-selective ALD has been previously demonstrated with patterns printed by ink-jet printing, micro-contact printing, directed self-assembly of templates, and a variety of other methods. However, there have been few techniques with the ability to directly 3-D print customizable patterns with sub-micron resolution, as traditional ink-jet printing is limited to a spatial resolution of ~20 microns. In this study, we demonstrate the use of electrohydrodynamic jet (e-jet) printing of polymers with sub-micron resolution [1], which can act as either inhibitors or promotors of ALD growth. The e-jet system allows for 3-D printing of polymers that pattern the surface chemistry by thermodynamically / kinetically activating or passivating local regions to nucleation of inorganic layers by ALD [2]. This enables bottom-up patterning of ALD growth, which can be integrated into 3-D nanosystems without the need for lithography or etching.

A variety of polymers were tested, demonstrating the ability to inhibit or promote the growth of ALD ZnO coatings on the surface by additive and subtractive printing approaches. Auger electron spectroscopy (AES), atomic force microscopy (AFM), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS) were used to perform compositional and elemental analysis of the patterned materials. After thin-film deposition by ALD, the electronic properties of the patterned films were characterized, demonstrating a pathway towards additive 3-D nanomanufacturing of customizable electronic devices.

1) M. S. Onses, E. Sutanto, P. M. Ferreira, A. G Alleyne, J. A. Rogers, *Small* **2015**, *11*, 4237–4266.

2) S. F. Nelson, C. R. Ellinger, D. H. Levy, *ACS Appl. Mater. Interfaces* **2015**, *7*, 2754–2759.

3:15pm **AS1-TuA-8 Selective Deposition of Silicon Nitride**,
***Han Wang**, B Hendrix, T Baum,* Entegris Inc.

Atomic layer deposition of SiN using SiI_4 and NH_3 was studied. The growth per cycle and initial nucleation of SiN films were analyzed as a function of the deposition temperatures and precursor pulse times on different substrates. The sequential reaction of SiI_4 and NH_3 showed longer nucleation delay on silicon oxide surfaces (native and thermal SiO_2) when compared to metal oxide (ZrO_2 and Al_2O_3) surfaces. This nucleation delay

decreased with the increased deposition temperature. By pretreating metal and silicon oxide surfaces with an NH_3 plasma, SiI_4 and NH_3 process showed no nucleation delay on the pretreated silicon oxide surfaces, while a significant delay was observed on the pretreated metal oxide surfaces. By using the definition of selectivity developed by Gladfelter [Chem. Mater. 5, 1372 (1993)], we have achieved $t_{S=0.90}$ = 18 Å for the process without NH_3 plasma pretreatment and $t_{S=0.94}$ = 74 Å for the process with NH_3 plasma pretreatment. This selectivity was not observed for pretreatment using H_2, N_2, or N_2-H_2 mixtures (50% N_2) plasma. Ex-situ XPS was used to determine the surface species with and without plasma pretreatments.

Area Selective ALD
Room Grand Ballroom H-K - Session AS2-TuA
Area-Selective ALD: Combinations with Etching

Moderators: Silvia Armini, IMEC, Dennis Hausmann, Lam Research

4:00pm **AS2-TuA-11 Area-Selective Deposition and Smoothing of Ru by Combining Atomic Layer Deposition and Selective Etching**, ***Martijn Vos,*** Eindhoven University of Technology, Netherlands*; S Chopra,* University of Texas at Austin*; M Verheijen,* Eindhoven University of Technology, Netherlands*; J Ekerdt,* University of Texas at Austin*; S Agarwal,* Colorado School of Mines*; E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

Area-selective ALD is expected to become a key technology for fabrication of nanoelectronics with sub-5 nm dimensions. The technology is nevertheless in an early stage of development, and one of the main challenges is to obtain a high selectivity.[1] The selective window can however be extended by introducing periodic etch steps that remove defects or nuclei from the non-growth area.[2]

In this work, it is demonstrated that Ru can be grown selectively on top of Pt or Ru (metal-on-metal), by integrating etch cycles into an ALD-etch supercycle. Furthermore, it is shown that this supercycle recipe simultaneously leads to smoothing of the Ru film on the growth area. Area-selective ALD of metal-on-metal is interesting for applications in semiconductor devices, and Ru is specifically relevant since Ru is being considered for the replacement of Cu in small dimension interconnects.

The optimal deposition temperature for the thermal Ru ALD process (without etching) was determined, by maximizing the difference in growth per cycle between growth on Pt and SiO_2. Even for the optimized temperature, the ALD process demonstrated a limited growth-selectivity between the two areas. A periodic etch cycle, consisting of an O_2 plasma exposure and a reducing H_2 dose, was therefore introduced to remove unwanted Ru nucleation from the SiO_2, allowing for area-selective deposition with improved selectivity. Both the etch time and frequency were varied to optimize the net growth rate on Pt, while maintaining a clean SiO_2 non-growth area. Using an etch cycle performed after every 100 ALD cycles, 8 nm was deposited with high selectivity on patterned Pt lines, demonstrating the potential of the approach. In addition, it is shown that the inclusion of etch cycles also has the benefit of smoothing of the Ru film, resulting in a lower surface roughness than for the ALD recipe itself. Finally, some guidelines will be discussed for extending the ALD-etch supercycle approach to other material systems.

[1] Mackus *et al*., Chem. Mater., 31, 1, 2019.

[2] Vallat *et al*., J. Vac. Sci. Technol. A., 35, 01B104, 2017.

4:15pm **AS2-TuA-12 Single Batch Strategies for the Development of an Area Selective Deposition Process with the Deposition/Etch Approach***,* ***Christophe Vallée,*** *M Bonvalot,* LTM-UGA, France*; R Gassilloud,* CEA-Leti, France*; V Pesce, A Chaker, S Belahcen,* LTM-UGA, France*; N Possémé,* CEA-Leti, France*; B Pelissier, P Gonon, A Bsiesy,* LTM-UGA, France

Several approaches are currently being investigated for the development of Area Selective Deposition (ASD) processes. For instance, the use of self-assembled monolayers (SAM) or block copolymers, processing temperatures promoting inherent selectivity, spatial ALD or selective ALD based on ABC-type cycles are common routes under study for this purpose [1-3]. The original approach developed in our group consists in taking benefit from an *in situ* etching step in a standard ALD cycle [4]. This deposition/etch approach is a simple and effective strategy and recently, two selective depositions have been obtained for two different plasma etching chemistries:

- First, selective deposition on metallic surfaces versus silicon-based surfaces (SiN, SiO_2 and Si) has been demonstrated in the case of Ta_2O_5 and TiO_2 by the application of an extra NF_3 plasma etching step to standard PEALD cycles [4-5];

- Second, geometric selective deposition (also called Topographically Selective Deposition) has been achieved on trench walls by the application of an extra Ar^+ sputtering step to standard PEALD cycles [6].

In this work, advantages and drawbacks of this deposition/etch approach to ASD processes will be discussed. The following issues will be addressed:

- What is the impact of the extra etching step on the material properties and on the overall throughput of the process? Are there any etching-induced damages to the substrate (etching, roughness…)?

- Does the deposition temperature have to be determined according to the boiling temperature of etching by-products?

- May the etching step induce any drift of the process?

By addressing these questions, the need for an appropriate specific design of the PEALD reactor will be emphasized so as to provide an efficient strategy for a precise control of plasma parameters. Special attention will be devoted to the role of medium energy ions in the plasma, as illustrated by the following two examples:

- At first, a new route for topographically selective deposition on top and bottom only of trenches will be discussed;

- Second, a surface selective deposition on SiO_2 surfaces versus metallic surfaces using the alternating PEALD/Atomic Layer Etching (ALE) approach will be shown.

[1] A. J. M. Mackus et al, *Chem. Mater.***31** (2019) 2-12

[2] G. N. Parsons, J. Vac. Sci. Technol. A 37 (2019) 020911

[3]R. Chen, H. Kim, P. C. McIntyre, and S. F. Bent, Appl. Phys. Lett. 84 (2004) 4017

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

[5] R. Vallat *et al*, *J. Vac. Sci. Technol. A***37** (2019) 020918

[6] A. Chaker *et al*, *Appl. Phys. Lett*. **114** (2019)

4:30pm **AS2-TuA-13 Surface Halogenation of Amorphous Carbon for Defect-free Area-Selective Deposition of Metal Oxides***,* ***Mikhail Krishtab***, KU Leuven, Belgium*; S Armini,* IMEC, Belgium*; S De Gendt,* KU Leuven/IMEC, Belgium*; R Ameloot,* KU Leuven, Belgium

The area-selective deposition (ASD) processes gained recently a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at nanoscale. As the critical dimensions approach few tens of nanometers, the precise positioning of a pattern becomes essential for reliably functioning devices or connections between them. The area-selective atomic-layer deposition (ALD) guided by the contrast in surface functionality allows to circumvent some of the lithography-related issues by introducing self-alignment of adjacent layers. However, the defectivity of typical ASD ALD processes relying on delayed nucleation on a non-growth area is one of the key concerns for the adoption of this technology. Among the strategies addressing the defectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

In this study, we examined the possibility to combine the two defect-reduction strategies by employing low power Cl_2 or CF_4 plasmas for both surface functionalization/re-functionalization and for removal of nuclei from a non-growth layer represented by amorphous carbon. We employed prototypical water-based metal oxide processes such as ALD ZnO (DEZ/H2O) and ALD TiOx (TiCl4/H2O) to demonstrate area-selective deposition on top of silicon oxide using both blanket films and patterns of amorphous carbon landing on a layer of thermal silicon oxide. At first, the plasma parameters were optimized to minimize etching of amorphous carbon and silicon oxide. Then the selectivity of the ALD processes under study was checked on the plasma halogenated amorphous carbon films using a standard ALD sequence and a sequence interrupted by the appropriate plasma treatment steps. While CF_4-plasma showed better performance in etching of metal oxide nuclei on top of amorphous carbon, the more hydrophobic fluorinated films exhibited inferior selectivity as compared to chlorinated amorphous carbon films for both types of ALD processes. In turn, Cl_2-plasma treated films of amorphous carbon demonstrated outstanding ALD ZnO growth inhibition along with lower tendency to formation of nucleation defects during ALD ZnO and ALD TiOx. The origin of the defects and of the observed differences in selectivity is discussed in the context of detailed surface composition analysis of the halogenated amorphous carbon films.

Area Selective ALD
Room Grand Ballroom H-K - Session AS2-TuA2
Late Breaking Abstracts

Moderators: Silvia Armini, IMEC, Dennis Hausmann, Lam Research

4:45pm **AS2-TuA2-14 Real-time Grazing Incidence Small-angle X-ray Scattering Studies of Indium Aluminum Nitride Growth*, Jeffrey M. Woodward, S Rosenberg,*** ASEE (residing at U.S. Naval Research Laboratory)*; S Johnson, N Nepal,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; K Ludwig,* Boston University*; C Eddy,* U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEp)[1], a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEp growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEp DA growth. To this end, we employ *in situ* grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving ternary InAlN surfaces as has been done previously for binary InN[2] and AlN[3].

Here we present *in situ* GISAXS studies of ALEp growth of InN, AlN, and a range of InAlN DAs on GaN (0001) substrates, which were performed at Brookhaven National Laboratory's NSLS-II using a custom reactor. The InAlN DAs studied include $In_{0.19}Al_{0.81}N$ (3 AlN cycles and 2 InN cycles per supercycle), $In_{0.5}Al_{0.5}N$ (1 AlN cycle and 3 InN cycles per supercycle), $In_{0.64}Al_{0.36}N$ (1 AlN cycle and 5 InN cycles per supercycle) and $In_{0.83}Al_{0.17}N$ (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, while others (19% and 64% In) exhibited 2D growth. *Ex situ* X-ray reflectivity data show evidence of phase separation in the 83% In DA.

[1] N. Nepal, V.R. Anderson, J.K. Hite, and C.R. Eddy, Thin Solid Films **589**, 47 (2015)

[2] J.M. Woodward, S.G. Rosenberg, A.C. Kozen, N. Nepal, S.D. Johnson, C. Wagenbach, A.H. Rowley, Z.R. Robinson, H. Joress, K.F. Ludwig Jr, C.R. Eddy Jr, J. Vac. Sci. Technol. A **37**, 030901 (2019)

[3] V.R. Anderson, N. Nepal, S.D. Johnson, Z.R. Robinson, A. Nath, A.C. Kozen, S.B. Qadri, A. DeMasi, J.K. Hite, K.F. Ludwig, and C.R. Eddy, J. Vac. Sci. Technol. A **35**, 031508 (2017)

5:00pm **AS2-TuA2-15 Expanding the Materials Library of Sequential Infiltration Synthesis: Conductive Indium and Gallium Oxides Grown in Polymers*, Ruben Waldman,*** University of Chicago*; N Jeon, D Mandia, O Heinonen, S Darling, A Martinson,* Argonne National Laboratory

Over the past decade, researchers have developed a deeper understanding of how the chemistry of ALD can be applied to polymeric substrates. Polymers are fundamentally unlike traditional ALD substrates in that precursors diffuse through the polymer and associate with functional groups that are distributed throughout the volume of polymer, rather than on a two-dimensional surface.

In one implementation of ALD in polymers called sequential infiltration synthesis (SIS), very long static exposures of precursors are used to enable diffusion into the polymer bulk. The published SIS materials library is quite limited compared to the broad ALD materials library. Aluminum oxide (Al_2O_3), as synthesized via SIS with trimethylaluminum (TMAl) and water, is by far the most studied system and has been utilized in applications ranging from lithography to oil sorption. Prior attempts to expand this library build upon on a primary SIS cycle of Al_2O_3 to act as a scaffold for subsequent synthesis of other materials. However, the insulating Al_2O_3 is detrimental to the properties of optoelectronically interesting materials. A detailed understanding of the physical and chemical processes of solvation, diffusion, and complexation between ALD precursors and polymer functionalities is required to engineer hybrid polymer-metal oxide devices and to develop a broader library of SIS materials.

Through a combined experimental and first principles computational study we have developed primary SIS processes for two previously unreported materials – indium oxide (In_2O_3) and gallium oxide (Ga_2O_3) – using congeners to TMAl (TMIn, TMGa) and water. Through Fourier transform infrared spectroscopy and density functional theory, we elucidate the binding configuration and affinity of TMAl, TMIn, and TMGa for the carbonyl functional groups in polymethylmethacrylate (PMMA). We find that the three form isostructural adducts, though TMAl binds three times more strongly, and observe that the kinetics of adduct formation/dissociation for TMAl are more than ten times slower than for TMIn or TMGa.

With detailed knowledge of the TMIn reaction kinetics we designed an SIS recipe with exposure and purge durations tuned to the time-scales of vapor diffusion in and out of the polymer film. This led to the templated synthesis of In_2O_3/PMMA hybrid films which are readily converted upon annealing to crystalline, conductive In_2O_3 films. Notably, we observe substantial SIS growth rates of In_2O_3 at 80 °C, well below what is possible with these precursors in ALD. This suggests that complexation with polymers can catalyze reactions, opening routes for further exploration of low temperature deposition processes.

5:15pm **AS2-TuA2-16 Highly Efficient and Stable Organic – Inorganic Halide Perovskite Solar Cells with ALD-grown Charge Transport Layers*, Hyunjung Shin,*** Sungkyunkwan University, Republic of Korea

$CH_3NH_3PbI_3$ with perovskite crystal structure has attracted considerable interest for high power conversion efficiency. Metal oxide grown *via* ALD provides pinhole-free uniform and dense films which are suited to function as passivation layer since ALD is deposited by self-limiting sequential chemical reaction. ALD chemistry for TiO_2, SnO_2, and ZnO are well known and the process requires relatively low deposition temperature as much as ~ 100 °C, which is applicable to deposit onto halide perovskite materials. In this presentation, we report highly efficient perovskite solar cells having a long-term stability that adapts uniform and dense inorganic charge transport layer (TiO_2, SnO_2, Al:ZnO, and NiO) grown by atomic layer deposition (ALD) at relatively low temperature. Ultra-thin un-doped NiO films were prepared by ALD with a highly precise control over the thickness. Thin enough (5 ~ 7.5 nm in thickness) NiO films with the thickness of few times of Debye length (1 ~ 2 nm for NiO) show enough conductivities achieved by overlapping space charge regions, which finally exhibited a highest PCE of 17.40 % with a negligible current-voltage hysteresis. Furthermore, highly dense inorganic electron transport layer (ETL) has been deposited onto perovskite using ALD process at relatively low temperature (100 °C). The devices shows excellent water-resistant properties and long-term stability at 85 °C under illumination compared to devices without ETL grown by ALD. **References** [1] H. Shin, et. al. "Perovskite Solar Cells with Inorganic Electron and Hole Transporting Layers Exhibiting Long – Term (≈ 500 h) Stability at 85 ° C under Continuous 1 Sun Illumination in Ambient Air", Adv. Mater., (2018) [2] H. Shin, et. al., "Atomic Layer Deposition of SnO Electron-Transporting Layer for Planar Perovskite Solar Cells with a Power Conversion Efficiency of 18.3 %" , Chem Comm (2019) [3] **Shin, H.** et. al. "Atomic Layer Deposition for Efficient and Stable Perovskite Solar Cells" *ChemComm* (2019)

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

AS-TuP-1 Laterally-Structured Dielectrics by Area-Selective Atomic-Layer-Deposition on 3D Substrates, ***Philip Klement****, D Anders, F Michel, J Schörmann, S Chatterjee,* Justus Liebig University Giessen, Germany

Industrial semiconductor fabrication combines lithography, etching, and deposition processes to create electronic devices. The quest for miniaturization of those devices has led to complex fabrication processes with multiple patterning and etching steps to achieve area-selective deposition. However, with conventional top-down fabrication reaching its limits in pattering resolution and alignment, a tool for bottom-up processing in advanced technology must deposit different combinations of materials area-selectively. Atomic-layer-deposition (ALD) is a technique for depositing high-quality, ultrathin films of dielectrics with the potential of area-selective deposition. It could reduce the number of manufacturing steps and allow for continued miniaturization, yet no area-selective deposition of lateral heterostructures has been realized.

Here, we show the successful direct patterned deposition of TiO_2 on complex SiO_2 substrates creating smooth surfaces of alternating dielectrics. Our approach demonstrates area-selective deposition on three-dimensional substrates, and we identify factors to consider that are not present in area-selective deposition on conventional two-dimensional substrates. We use a combination of electron beam lithography using a polymer mask, ion beam etching, plasma treatment, and ALD similar to established semiconductor fabrication processes to realize lateral heterostructures of dielectrics. Several process parameters were varied, and their effect on the resulting structure was investigated by atomic force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. We investigated different polymer mask surfaces and precursor diffusion in terms of area-selective deposition, and found that a number of factors must be considered in design, patterning, and deposition to achieve reproducible results. Our work enables the realization of lateral heterostructures of dielectrics as building blocks for advanced technology applications.

AS-TuP-2 Light Assisted Area Selective Atomic Layer Deposition on Plasmonic Nanoantennas, ***Chengwu Zhang****, T Gao, B Willis,* University of Connecticut

Plasmonic nanoantennas, especially with gaps less than 10 nm, can greatly enhance electric fields through excitations of surface plasmons, which are collective oscillations of electrons excited by light. Arrays of plasmonic nanoantennas can be designed to concentrate and manipulate light at the nanoscale, and have wide applications such as surface enhanced spectroscopy, photo-driven chemical conversion, and optical information processing. Atomic layer deposition (ALD) is a thin-film deposition technique capable of producing conformal thin films with precise control of thickness and composition at the atomic level. Area selective ALD provides a way to precisely tune nanogaps to enhance their optical and electronic properties. The optical properties of plasmonic nanostructures offer the possibility to enhance selective growth through resonant excitations. In this work, we investigate the effect of light in area selective ALD on plasmonic nanoantennas.

We present a case study of Cu area selective ALD on Pd nanoantennas. The sizes of antenna dimers range from 25 nm to 200 nm, with 20 nm gaps. The gaps are measured and compared before and after thermal ALD with and without light irradiation. Results show GPC (growth per cycle) is enhanced at lower temperatures using irradiation, which yields better selectivity. As an example, for nanoantennas with lengths of 75 nm and widths of 25 nm, ALD growth at 150℃ with light yields almost the same GPC as 230℃ without light. Compared with thermal ALD, only 1/3 number of cycles are required for the same growth with irradiation. Using various nanoscale antenna designs and array configurations, we analyze the role that plasmonic heating or hot electrons may contribute to the enhanced growth.

AS-TuP-3 Area-Specific Atomic Layer Deposition (ALD) of Cobalt As Mediated by Thermally Induced Dehydrocoupled Self-Assembled Monolayers (SAMs), ***Barry Arkles****, J Goff, C Brick,* Gelest, Inc.*; A Kaloyeros,* SUNY Polytechnic Institute

Organic trihydridosilanes can provide an elegant route for generating self-assembled monolayers (SAM)s by vapor phase transport on a variety of substrates. Under mild conditions, these precursors can be made to interact with a variety of clean metal and hydrogenated metalloid surfaces, including those of interest for nanoscale integrated circuitry (IC) applications, such as titanium, copper, and silicon, to form near-zero-thickness SAMs. As shown in the figure below, the resulting SAMs can be customized with specific functionality (depending on the choice of the R substituent) to activate or deactivate subsequent ALD Co on the underlying substrate of choice, leading to area-specific Co deposition. In this work, negative and positive ALD Co protocols under low substrate temperature conditions will be presented and discussed.

AS-TuP-4 Investigation of *In-situ* Surface Cleaning of Cu Films using O_3/O_2 and N_2H_4, ***Su Min Hwang****, A Kondusamy, Q Zhiyang, H Kim, L Peña, K Tan, J Veyan,* University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; J Kim,* University of Texas at Dallas

Copper is widely used in semiconductors as interconnects due to its low resistivity, high resistance to electromigration, low temperature coefficient of resistance, and good thermal stability.[1] Recent demonstration of atomic layer deposition (ALD) of Cu thin films is expected to overcome the limitations of the PVD process and could be used to deposit a highly conformal film over high-aspect ratio structures with precise thickness control. Several processes on ALD Cu have been reported requiring an additional reduction step to obtain metallic Cu.[2] Therefore, it is imperative to explore reducing agents capable of reducing the oxide on Cu at low temperatures. Among the various available reducing agents, N_2H_4 (Hydrazine) can be used in the reduction of copper oxide due to its higher reduction capability.[3] Inspired by Hydrazine's unique characteristics, we explore the feasibility of vapor-phase reduction of copper oxide using N_2H_4 to achieve an ideal metallic Cu film in an ALD environment. Additionally, a detailed *in-situ* surface analysis of the reduction with N_2H_4 has not been reported yet.

In this work, Cu samples were oxidized using an O_3/O_2 mixture, followed by N_2H_4 using a rapid thermal ALD system to investigate the reduction effectiveness of N_2H_4. From the XPS analysis, Cu samples treated with O_3/O_2 showed the diffusion of oxygen into the sample and the formation of Cu_2O layer that is approximately 4 nm thick. With N_2H_4 treatment, a significant amount of copper oxide was reduced to metallic copper with approximate thickness of 1 nm, the comparable reduction capability of N_2H_4 agent. In addition, *in-situ* reflection absorption infrared spectroscopy (RAIRS) was employed to elucidate the individual surface chemistry of copper films during the oxidation (O_3/O_2) and reduction (N_2H_4) step. The detailed experimental results will be presented.

This work is partially supported by Rasirc Inc. by providing N_2H_4. We also acknowledge TMEIC (Toshiba Mitsubishi-Electric Industrial Systems Corporation) for providing the O_3 generator.

[1] R.P. Chaukulkar, N.F.W. Thissen, V.R. Rai, and S. Agarwal, J. Vac. Sci. Technol. A **32**, 01A108 (2014).

[2] L.F. Pena, J.F. Veyan, M.A. Todd, A. Derecskei-Kovacs, and Y.J. Chabal, ACS Appl. Mater. Interfaces **10**, 38610 (2018).

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AS-TuP-5 Area-Selective Deposition of SiO_2 based on Spatial ALD with Interleaved Etching Steps to Obtain High Selectivity, ***Alfredo Mameli****,* TNO/Holst Center, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands*; P Poodt,* TNO/Holst Center, Netherlands

Area-selective atomic layer deposition (AS-ALD) has been envisioned as a potential technological solution for advanced patterning. However, the selectivity that can be obtained is often very limited and the throughput of most AS-ALD methods is low, which hampers its industrial acceptance.[1,2] In this work, we present a process for AS-ALD of SiO_2 using intermittent plasma etching steps to obtain high selectivity.[3] At the same time, the deposition process itself is performed in a spatial ALD mode at atmospheric pressure that allows for achieving high throughput.[4]

AS-ALD of SiO_2 on a pre-patterned substrate with SiO_2 and ZnO was demonstrated using a chemoselective inhibitor that chemisorbs preferentially on the non-growth area (ZnO) while it allows for depositing SiO_2 on the growth area (SiO_2). In order to obtain high selectivity, a blanket

fluorocarbon plasma etching step was interleaved after every 110 ALD cycles. This way, up to ~ 30 nm-thick selective SiO_2 deposition was demonstrated, as shown in Figure 1 of the supplemental PDF file. Furthermore, X-ray photoelectron spectroscopy was carried out to verify the selectivity of the process. No Si was detected on the non-growth area, demonstrating the high selectivity of this process.

The process presented in this work combines selective inhibitor chemisorption, plasma-based spatial ALD at high deposition rates and plasma etch-back steps to correct for selectivity loss. Being compatible with roll-to-roll and sheet-to-sheet concepts, this approach can enable high-throughput AS-ALD on large-area and flexible substrates as well.

[1] A. Mameli et al., *ACS Nano*, **2017**, 11, 9303-93

[2] F.S.M. Hashemi et al., *ACS Nano*, **2015**, 9, 8710-8717

[3] R. Vallat et al., *JVSTA*, **2017**, 35, 01B104

[4] P. Poodt et al. *JVSTA*, **2012**, 30, 01802(1-10)

AS-TuP-6 Defect Mitigation Solution for Area-Selective Atomic Layer Deposition of Ru on TiN/SiO_2 Nanopatterns, *J Soethoudt,* KU Leuven – University of Leuven/IMEC, Belgium*; F Grillo,* ETH Zurich, Switzerland*; E Marques, R van Ommen,* Delft University of Technology, Netherlands*; B Briggs, H Hody, V Spampinato, A Franquet, B Chan,* ***Annelies Delabie,*** IMEC, Belgium

Area-Selective Deposition (ASD) receives increasing attention as a bottom-up approach for nanopatterning. Implementation of ASD is however limited by undesired particle growth on the non-growth surface. This work provides a demonstration of defect mitigation strategies based on insight into the particle growth mechanism on the non-growth surface. Ru is selectively deposited by 1-(ethylbenzyl)-1,4-(ethylcyclohexadienyl)ruthenium (EBECHRu) and oxygen atomic layer deposition on TiN/SiO_2 nanopatterns pretreated with dimethylamino-trimethylsilane. This material system is relevant for a tone inversion patterning application, where a hard material (Ru) is selectively deposited inside holes in a soft material (SiO_{-2}) which is more straightforward than patterning the hard material directly[1]. Ru films are selectively deposited on TiN, while particle growth is observed on dielectrics (Figure 1a). The thickness of the selectively deposited Ru layer on TiN is independent of feature dimensions in the entire investigated size range of 90µm-25nm (Figure 1b). We propose two strategies to mitigate defectivity based on the first stages of EBECHRu/O_2 growth on dielectrics. Initially, the Ru particles are too small to catalytically dissociate oxygen, thereby suppressing direct deposition on the particles[2]. Ru particles at first grow only through surface diffusion and coalescence until they reach a sufficient size for catalytic O_2 dissociation, at which point the particles start to rapidly grow through direct deposition on the particles. A first defect mitigation strategy employs the initial growth regime in which particles are smaller compared to the ASD-grown film. During this regime, the particles can be fully etched with limited thickness reduction of the ASD Ru layer. Self-Focusing Secondary Ion Mass Spectrometry (SF-SIMS) is used as a probe for ASD defectivity due to its low limit of detection and the potential to analyse over 10^4 structures simultaneously[3,4]. A window was identified in which an ASD Ru layer fully covers the growth surface while no defects are observed by SF-SIMS (Figure 2). The second defect mitigation strategy limits the diffusion-mediated growth of particles during the initial regime, thereby extending its length and significantly enhancing selectivity (Figure 3). The size-dependent nanoparticle reactivity in EBECHRu/O_2 ALD suppresses particle growth on the non-growth surface. As such, particles can be completely etched while retaining the integrity of the ASD pattern.

[1]B. Briggs et al., *CSTIC* (2018)

[2]J. Soethoudt et al., *Adv. Mater. Int.* (2018)

[3]A. Franquet et al., *App. Surf. Sci.* (2016)

[4]V. Spampinato et al., *App. Surf. Sci.* (2019)

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— Y —
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