## Area Selective ALD
## Room On Demand - Session AS1
### Selective ALD by Area-Activation

**AS1-1 Area-Selective Atomic Layer Deposition Patterned by Electrohydrodynamic Jet Printing for Additive Nanomanufacturing of Functional Materials and Devices*, **Tae Cho**, N. Farjam, C. Allemang, C. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. Peterson, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Personalized health care has lead to an increase in demand for customization of integrated nanosystems. However, existing additive nanomanufacturing techniques are often restricted by long processing times and/or strict material requirements. For instance, electrohydrodynamic jet (EHD) printing allows for fast and versatile printing down to 30 nm feature sizes, but requires special attention to the physical/chemical properties of the ink. To expand on this nanoprinting approach, we have demonstrated that by patterning polymer geometries, EHD can be used to locally activate/deactivate ALD growth [1,2].

In this study, we combined area-selective atomic layer deposition (AS-ALD) and EHD to pattern inhibitor polymers with sub-micrometer resolution and high line speeds [2]. This allows patterning of ZnO, $Al_2O_3$, $SnO_2$, and their ternary combinations with tunable geometry and elemental composition. With additive EHD printing, polyvinylpyrrolidone was printed with an average linewidth of 312 nm to deactivate the surface to ALD growth. Furthermore, using solvent-based subtractive EHD printing to dissolve polymethylmethacrylate [1], an average linewidth of 9 µm region was patterned to activate the surface.

Using this technique, a bottom-gate, top-contact thin-film transistor, with an on/off current ratio of greater than $10^5$,was fabricated using zinc-tin-oxide (ZTO) as the semiconductor and aluminum-doped zinc oxide as the source and drain electrical contacts. We have also demonstrated that by combining thermal and plasma-enhanced ALD processes, ZTO film density can be increased, which resulted in the highest reported $\mu_{FE}$ of ~22 $cm^2V^{-1}s^{-1}$ after post-deposition anneal at 400 °C [3]. However, due to the thermal budget of the inhibitor polymers used in AS-ALD–EHD process, a low ALD deposition temperature was used, yielding lower mobility compared to the thermal-plasma ALD device. Therefore, to improve device performance, we have studied the effect of the oxidant ($H_2O$, $O_3$, and plasma) and deposition temperature on the ALD selectivity and device performance. This technique can be further used to print on nonplanar and/or flexible substrates, without the need for traditional lithography.

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[1] N. Farjam, T. H. Cho, N. P. Dasgupta, K. Barton, *Appl. Phys. Lett.* **117**, 133702 (2020)

[2] T.H. Cho, N. Farjam, C. R. Allemang, C. P. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. L. Peterson, K. Barton, N. P. Dasgupta, *ACS Nano* **14**, 17262 (2020)

[3] C. R. Allemang, T. H. Cho, O. Trejo, S. Ravan, R. E. Rodríguez, N. P. Dasgupta, R. L. Peterson, *Adv. Electron. Mater.***6**, 2000195 (2020)

**AS1-2 Surface-Activated Area-Selective Atomic Layer Deposition of Palladium***, **Himamshu Nallan**, X. Yang,* University of Texas at Austin*; B. Coffey,* Lam Research Corporation*; J. Ekerdt,* University of Texas at Austin

Flexible electronics and next-generation roll-to-roll nanomanufacturing rely on the use of polymeric substrates, which constrain processing temperatures. In addition to typically operating a low thermal budget, ALD can provide atomic-level control, making it a suitable method of deposition for these applications. In this work, we present an area-selective ALD (AS-ALD) route to grow difficult-to-nucleate metals that promises to mitigate the need for post-deposition removal of any metal that grows non-selectively.

The area-selective deposition of palladium metal uses palladium(II) hexafluroacetylacetonate and $H_2$ at low temperature (≤150 °C). There is a significant nucleation delay during the deposition of Pd with these coreactants on various metal-oxide substrates due to the low reactivity of the $H_2$ molecule with $Pd(hfac)_2$ as well as the Hhfac reaction product inhibiting oxide surface sites. Typically, a high deposition temperature or hydrogen plasma is employed to facilitate Pd film growth. Here we report an alternative route to enhancing palladium deposition and conferring selectivity by employing a pre-patterned metallic seed layer. First, AS-ALD of nickel(II) oxide is carried out on pre-patterned $sp^3$ carbon-rich resist using bis(N,N'-di-tert-butylacetamidinato)nickel(II) and $H_2O$ as coreactants at 200 ºC to yield conformal, carbon-free oxide films, with high selectivity and no nucleation delay. Subsequently, the nickel(II) oxide films are reduced with atomic and/or molecular hydrogen to nickel(0), which readily facilitates the surface dissociation of $H_2$ and thereby enhances the deposition of Pd, defining a route to selective deposition. As only surface nickel(0) provides nucleation enhancement for metal-on-metal deposition, partial, superficial reduction of the nickel(II) oxide film is sufficient. In this way, the selectivity of the oxide deposition process is conferred to palladium deposition as well. In-situ x-ray photoelectron spectroscopy is used to determine the presence and oxidation states and film stoichiometry of palladium and nickel. Ex-situ x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

**AS1-3 In-Situ and in-Vacuo Studies on Area Selective Atomic Layer Deposited Ruthenium Films on Silicon and Silicon Oxide***, **Sebastian Killge**, J. Reif,* Technische Universität Dresden, Germany*; M. Knaut, M. Albert,* Technische Universität Dresden, Institute of Semiconductor and Microsystems (IHM); Chair of Nanoelectronics, Germany*; J. Bartha, T. Mikolajick,* Technische Universität Dresden, Germany

We present a thermal activated inherent area selective atomic layer deposition (*thALD*) of ruthenium (*Ru*) on crystalline silicon (*cSi*) wafer and silicon oxide (*$SiO_2$*)interfaces.

The selective deposition is based upon the inhibited nucleation of ruthenium on oxide surfaces such as $SiO_2$ compared to Si and metal surfaces. ThALD ruthenium (5-20 nm thick) deposited with the organometallic precursor ECPR [(ethylcyclopenta-dienyl)(pyr-rolyl) ruthen-ium(II)] and molecular oxygen [1, 2] on 4 inch silicon [100] wafers with a pattern of cSi dipped by diluted hydrofluoric acid (*HF*), and native silicon oxide (1.8 nm).

In our experiments, the pattern on the wafer was created by lithography with AZ® 5214 E resist. A dip with 0.5% HF (30 s) was used to remove the native oxide film on cSi and to create a hydrogen-terminated surface. Immediately afterwards, the resist was stripped by a treatment with acetone, 2-propanol, and clean water (conductivity 0.05 µS/cm). After drying, the wafer was transferred into ALD tool for deposition within less than 5 minutes.

As shown in [2-4], the initially incubating and nucleation periods strongly depend on the deposition temperature. On HF-dipped cSi after a nucleation period of 10 ALD cycles a steady-state Ru-on-Ru(Ox) growth with a GPC of ca. 0.9 Å was observed (Fig. 1) at 180 °C. In the linear steady-state region the GPC was nearly independent on the deposition temper-ature [2]. On native $SiO_2$, only isolated islands of Ru were formed in negligible quantity after 150-180 ALD cycles, consisting of non-stoichiometric Ru / Ru(Ox). Here, growth started after 180 ALD cycles, whereas on HF-dipped Si a 16 nm thick Ru film (Rs= 14,2 Ω/□; ρ= 22,72 µΩ*cm) has been deposited already (Fig. 2). A higher quality of selectivity became be achieved by combining ALD with selective etching using an $O_2$ or $O_3$ purge after a certain number of ALD cycles (Fig. 3). As we demonstrated earlier [1, 2], purge steps with molecular hydrogen (*$H_2$*) during Ru-ALD can prevent blister formation.

**AS1-6 Nucleation and Growth in Localized Thermal Atomic Layer Depostion***, **Bart de Braaf**, K. Storm,* Eindhoven University of Technology, Netherlands

We explore the possibility of achieving area selective ALD by modifying the temperature profile on the substrate. The technique keeps the majority of the substrate at a low temperature, suppressing the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. A practical example of this technique is the ALD process of $Si_2H_6$(1). Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized dots and lines given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the domain deposited on the substrate.

Bibliografie

1. *Ar+-laser-assisted subatomic-layer epitaxy of Si.* **Y. Suda, M. Ishida, M. Yamashita.**1996, Journal of Crystal Growth, pp. 672-680.

## Area Selective ALD
## Room On Demand - Session AS2
## Selective ALD by Area-Deactivation

**AS2-1 Gradient Area Selective Deposition using Ti Precursor Inhibitor for Seamless Gap-filling in 3D Nanostructure Pattern***, **Chi Thang Nguyen**,* Incheon National University, Korea (Republic of)*; E. Cho,* Samsung Electronics, Korea (Republic of)*; J. Park,* Hongik University, Korea (Republic of)*; B. Gu,* Incheon National University, Korea (Republic of)*; B. Shong,* Hongik University, Korea (Republic of)*; H. Lee,* Incheon National University, Korea (Republic of)

Atomic layer deposition (ALD) is a thin film deposition technique with excellent uniformity and conformality at nanoscale due to its unique surface self-saturated reactions of precursors and counter reactants. However, the isotropic growth of ALD is one of the bottlenecks to enable the seamless gap-filling in high aspect ratio structures, such as holes and trenches because the opening of structures is closed off at a certain thickness, resulting in formation of a void. In this work, we introduce an area-selective ALD (AS-ALD) process to realize seamless deposition in 3D nanostructures by using a gradient adsorption of a Ti source precursor inhibitor namely $TiCp^*(OMe)_3$. The $TiCp^*(OMe)_3$ inhibitor can block the growth of TiO2 ALD (using Tetrakis(dimethylamido)titanium-TDMAT precursor) up to 900 cycles (ca. 50 nm) with a high selectivity of ca. 91.3 %. For the gradient AS-ALD, the density of inhibitor adsorption inside 3D structures is controlled by exposure of the $TiCp^*(OMe)_3$ inhibitor, and the deposition of $TiO_2$ is inhibited in the following $TiO_2$ ALD depending on the surface concentration of the inhibitor. The results show the ability to control the growth of $TiO_2$ ALD in the hole pattern (aspect ratio =16). The gap can be filled up from bottom to determined position inside hole without any seams in the centerline. Theoretical calculations by Density functional theory (DFT), Monte Carlo (MC) simulation show high consistency with the experimental results. The concept of gradient AS-ALD could be extended to other ALD materials system for better and simplified process in many various applications.

**AS2-4 Selectivity Loss Mechanisms in $TiO_2$ Area Selective Deposition on Dimethylamino-Trimethylsilane Passivated $SiO_2$***, **Rachel Nye**,* North Carolina State University*; K. Van Dongen, J. Clerix,* KU Leuven, Belgium*; G. Parsons,* North Carolina State University*; A. Delabie,* KU Leuven, Belgium

Titanium oxide ($TiO_2$) area-selective deposition (ASD) has been studied for applications such as hard masks for tone inversion, dielectric layers, solar cells, and photocatalysis due to the etch resistance, high dielectric constant, and high refractive index of $TiO_2$. While these studies[1] have successfully demonstrated several nanometers of selective deposition using various passivation, activation, and defect mitigation techniques, there is still work needed to understand selectivity loss mechanisms in order to further expand selectivity windows to reach commercial requirements. Herein we evaluate selectivity loss mechanisms of $TiO_2$ deposited on trimethyl-silane passivated $SiO_2$ substrates from $TiCl_4/H_2O$.

Dimethylamino-trimethylsilane (DMA-TMS) passivates $SiO_2$ substrates with a 300 s exposure at 250 °C while Si, $TiO_2$, TiN, and Ru surfaces remain unaffected.[2] This DMA-TMS passivated $SiO_2$ limits $TiO_2$ surface coverage to ~5% after 100 cycles (3.8 nm on the growth surface) at 150 °C, as characterized by scanning electron microscopy (SEM) and Rutherford backscattering spectrometry (RBS) (Fig. 1).

Nuclei on the non-growth surface were analyzed with SEM and atomic force microscopy (AFM) to gain insight on nucleation mechanism, adsorption kinetics, and possible impact of diffusion (Fig. 2). Particle size distributions (PSDs) reveal a high concentration of small nuclei even for high cycle numbers. This indicates new nuclei generation on the non-growth surface during deposition. Kinetic modeling[3] was employed to fit experimental data according to this information using an estimated site generation rate of $4.6x10^{-5}$ sites cm$^{-2}$ cycle$^{-1}$ and a 30-cycle nucleation delay. Modeling results correspond to a thickness of ≈4 nm $TiO_2$ while maintaining 90% selectivity ($t_S = 0.9 = 4.02$ nm).* Furthermore, we compare PSDs at low (150 °C) and high (300 °C) deposition temperatures to evaluate changes in species diffusivity and loss of effectiveness in the passivation layer. Finally, this insight is applied to develop techniques for extending $TiO_2$ selectivity windows, including repeated passivations and periodic etching to mitigate defects. The improved understanding on $TiO_2$ selectivity loss identifies effective strategies to increase selectivity to reach advanced technology nodes.

**AS2-7 Area-Selective Atomic Layer Deposition of $Al_2O_3$ on $SiO_2$ Vapor-Functionalized with Small-Molecule Aminosilanes***, **Wanxing Xu**,* Colorado School of Mines, USA*; P. Lemaire, K. Sharma, D. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines, USA

With feature dimensions of state-of-the-art semiconductor devices moving toward the 5 nm node and beyond, device fabrication based on top-down approaches is becoming ever more challenging. Recently, area-selective atomic layer deposition (ALD) has evolved as a promising method to fabricate well-defined patterns from the bottom-up with atomic-scale accuracy. Within the different approaches for area-selective ALD, the preparation of patterned substrates with material-selective organic functionalization offers a promising direction for achieving self-aligned patterns over large areas. In this study, we focus on area-selective ALD of $Al_2O_3$ on functionalized $SiO_2$ with small-molecule aminosilanes through the vapor phase. Using *in situ* optical surface diagnostics, we investigate the atomistic-scale mechanism that leads to the reaction of the ALD precursors with the functionalized $SiO_2$ surface.

To inhibit the ALD of $Al_2O_3$ on $SiO_2$, $SiO_2$ substrates were exposed to bis(dimethylamino)dimethylsilane and (*N*, *N*-dimethylamino)trimethylsilane through the vapor phase. *In situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy shows that the aminosilanes react with almost all of the surface –OH groups, thereby rendering the surface unreactive toward dimethyl aluminum isopropoxide (DMAI), which was used at the aluminum precursor in conjunction with and $H_2O$. *In situ* ATR-FTIR spectroscopy was also used to monitor the reactions on the $SiO_2$ surface during $Al_2O_3$ ALD while film growth was monitored using *in situ* four-wavelength ellipsometry. Our experiments show that growth initiation on the functionalized $SiO_2$ surface may occur due to DMAI molecules that remain strongly bound to the $SiO_2$ surface after the purge step, suggesting that the growth on functionalized $SiO_2$ surface could be further inhibited by lowering the precursor dose (see Figure 1). We further show that the growth inhibition of an additional 20 ALD cycles is obtained on functionalized $SiO_2$ when the DMAI dose dropped from 3.2 Torr·s to 0.4 Torr·s (see Figure 2). Finally, we show that the less reactive precursor, DMAI, leads to better growth inhibition on functionalized $SiO_2$ compared to trimethylaluminum.

## Area Selective ALD
## Room On Demand - Session AS3
## Inherently Selective Processes

**AS3-1 Impact of Precursor Structure on the Initial Growth Trends of Atomic Layer Deposited $Al_2O_3$ Films on Chemical Oxide and Hf-last Silicon***, **Holger Saare**, G. Parsons,* North Carolina State University

Aluminum oxide thin films are utilized in numerous applications, such as gate oxides, heat sinks, barrier materials, and more. Atomic layer deposition (ALD) of $Al_2O_3$ using trimethylaluminum (TMA) as a precursor is one of the most extensively studied ALD processes, owing to its high vapor pressure, high reactivity, and self-terminating reactions. However, for area-selective deposition (ASD) applications, such as next-generation nanopatterning, this reactivity leads to poor selectivity, as TMA rapidly reacts with most surfaces. Thus, alternative precursors for the selective deposition of $Al_2O_3$, which result in selectivity between different surfaces while maintaining high film quality, need to be considered.

In this work we compare initial growth trends of $Al_2O_3$ ALD on hydrogen-terminated Si (Si-H) vs hydroxyl-terminated Si (Si-OH) surfaces using three different Al precursors and $H_2O$ as the oxygen source. Triethylaluminum (TEA), dimethylaluminum chloride (DMAC), and TMA are chosen as the Al precursors due to comparable variations between their structures. This enables us to determine the effects that alkyl ligand length and the presence of chloride groups have on the growth selectivity. The growth trends are studied in the temperature range of 150-250 °C and characterized using *in-situ* spectroscopic ellipsometry (SE) and *in-situ* Auger electron spectroscopy (AES).

Measured thickness evolution exhibits similar behavior for all three precursors as shown in Figure 1. On the Si-OH starting surface, the first cycle shows an accelerated growth rate due to higher precursor uptake and then proceeds in a steady-state manner characteristic to ALD. The resulting growth rates are 0.13, 0.11, and 0.10 nm/cycle for TMA, TEA, and DMAC, respectively. Meanwhile, the growth on the Si-H surface exhibits a delay due to the lack of hydroxyl groups. The growth rate accelerates as more nuclei are deposited and eventually reaches steady-state growth rate as the islands coalesce into a uniform film. While TMA results in the highest growth rates, it leads to the lowest selectivity throughout the cycles as shown in Figure 2. The highest selectivity is achieved using TEA, owing to low rate of nucleation on the Si-H surface. Chemical analysis using AES confirms the growth trends present and shows that the steady-state growth rate is decreased due to -$CH_3$ groups present on the surface.

These results provide vital insight into the importance of precursor selection for area-selective ALD applications and open the pathway to realizing selective $Al_2O_3$ deposition based on inherent substrate selectivity.

**AS3-2 Inherently Area-Selective Atomic Layer Deposition for High-*K* Dielectrics by Catalytic Local Activation*, Jeong-Min Lee*,** *H. Kim, J. Ahn, W. Kim,* Hanyang University, Korea

In modern technologies, area-selective atomic layer deposition (AS-ALD) which allows for precise pattern placement with nanoscale dimensions through an additive approach has attracting tremendous interests as a solution to implement the bottom-up nanopatterning for the future semiconductor fabrication. More recently, inherent AS-ALD, which exhibits substrate-dependent deposition selectivity without the use of surface-deactivating molecules, can be expected to offer enormous advantages over conventional inhibitor-assisted AS-ALD in terms of more simplified process and avoiding inhibitor-associated contamination issues. Therefore, we report a methodology for achieving inherently selective deposition of high-k dielectric thin films by catalytic local activation on noble metal substrate. In this work, we demonstrate that AS-ALD of $Hf_{1-x}Zr_xO_2$ films can be achieved by chemo-selective adsorption of precursors which arises from catalytic dissociation of a coreactant molecules on noble metal surfaces like Pt and Ru. For this purpose, $O_2$ gas was utilized as a mildly oxidizing coreactant and tris(dimethylamido)hafnium/zirconium-cyclopentadienide (CpHfZr) precursors which require strong oxidizing agents were used to deposit selective $Hf_{1-x}Zr_xO_2$ thin films. Finally, we successfully achieved inherent selectivity greater than ~5 nm on both blanket- and Si/Pt-patterned substrates. This approach for achieving inherent selectivity expands the potential utility of bottom-up nanopatterning processes for next-generation nanoelectric applications.

**AS3-3 Integration of Two Atomic Layer Depositions in a Sequence for Area Selective Deposition of Two Materials*, Seung Keun Song*,** *J. Kim, G. Parsons,* North Carolina State University

The semiconductor industry is now entering the new era of ~3 nm patterning in electronic device manufacturing, leading to many challenges in high volume manufacturing. To achieve satisfactory quality in nanoscale device features, in addition to extreme UV (EUV) lithography, “bottom-up” growth of thin films through area selective deposition (ASD) is becoming a key technique in the manufacturing flow.

ASD deposits a thin film of material on a target region of a substrate while maintaining clean surfaces on adjacent, non-growth regions by translating chemical surface information. ASD methodologies have been demonstrated in roughly two ways, namely 1) locally pre-modifying the substrate to passivate or activate one region or/and 2) integrating etch-back/passivation steps in deposition cycles to suppress unfavorable growth. Many ASDs have focused on selectively depositing one material on one target surface. However, in this talk, we report ASD of two materials ($TiO_2$ and W) on two different regions ($SiO_2$ and Si-H) of one substrate by integrating two ASDs into one process sequence.

Previously, our group reported an ALD/ALE process for $TiO_2$ ASD on $SiO_2$ vs Si-H. We also reported W ASD on Si-H vs $SiO_2$ using W ALD ($SiH_4$/$WF_6$), which is reverse selectivity compared to the $TiO_2$ ASD. Herein we examine two scenarios for the integration of two ASD processes ($TiO_2$ ASD and W ASD) to achieve ASD of two materials without significant interference, which are W 1st (W ASD + $TiO_2$ ASD) and $TiO_2$ 1st ($TiO_2$ ASD + W ASD). (Fig. 1) After careful analysis of in situ quartz crystal microbalance (QCM) for two scenarios, $TiO_2$ 1st case is confirmed as a feasible integration sequence for ASD of $TiO_2$ and W on $SiO_2$ and Si-H, respectively. After the integrated sequence of $TiO_2$ ALD/ALE and W ALD, ~5 nm of $TiO_2$ and ~7 nm of W thin films are confirmed by TEM. Furthermore, we also find that intermediate treatment such as HF dip between ASDs helps W growth on Si-H by regenerating hydrogen terminations.

Beyond the demonstration of selective deposition, these results also explain deposition difference on non-patterned vs patterned substrate after the integrated ALD sequence. We believe these findings give an important insight into integrating two or more selective processes including ALD, ALE, CVD, and CVE for true bottom-up nanofabrication.

**AS3-4 Substrate Dependent Absorption of Volatile Antimony Pentachloride during Vapor Phase Poly(3,4-ethlenedioxythiophene) Polymerization*, JUNGSIK KIM*,** *G. Parsons,* North Carolina State University

Bottom-up processing has drawn attention in the field of nanoelectronics due to its capability to produce transistors with feature size less than 5 nm. Based on inherent chemical selectivity on different surfaces, area-selective deposition (ASD) is the primary technique to obtain bottom-up 3D patterning. Although many studies regarding ASD of inorganic materials have been addressed, there are few studies on ASD of polymers. Selective polymer deposition could play an important role in nucleation inhibitors/initiators, blocking masks, and air-gap applications. We have previously reported ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) by o-MLD using a volatile liquid $SbCl_5$ oxidant and 3,4-ethylenedioxythiophene monomer (EDOT).[1] During the o-MLD process, PEDOT showed selective growth on thermally grown silicon dioxide ($SiO_2$) vs hydrogen-terminated silicon (Si-H).

In this work, the mechanism of PEDOT ASD on $SiO_2$ and Si-H was studied. Compared to $SiO_2$ substrates, PEDOT showed a nucleation delay on Si-H surfaces. We believe that the growth inhibition on Si-H is due to the $SbCl_5$ reaction with Si-H surfaces. As shown in **Figure 1**, thermodynamic calculation shows that the $SbCl_5$ oxidant is readily reacted with Si, whereas no reaction is observed on $SiO_2$ surfaces. To clearly understand the $SbCl_5$ dose effects on PEDOT selectivity, different $SbCl_5$ exposure conditions were systematically investigated. Using the oMLD process, we demonstrated ~20 nm of PEDOT ASD on $SiO_2$/Si-H patterned substrates as shown in **Figure 2**.

These results suggest that minimizing $SbCl_5$ exposure is a key factor into enhancing PEDOT selectivity. In this regard, a fast net growth rate by the CVD process was employed to improve the selectivity. By decreasing the $SbCl_5$ exposure time with the fast growth rate, unfavorable nucleation on Si-H was effectively controlled, leading to better PEDOT ASD compared to MLD. An analytical nucleation model was implemented to quantify ASD between MLD and CVD processes. These studies give an important insight into developing conjugated polymer ASD and play a pivotal role in improving the ASDs.

**AS3-7 Inherent Selective CVD of Amorphous $HfO_2$/$TiO_2$ Nanolaminate for Nanoscale Patterning*, Yunil Cho*,** *J. Huang,* University of California at San Diego*; C. Ahles,* University of California San Diego*; K. Wong, S. Nemani, E. Yeah,* Applied Materials*; A. Kummel,* University of California at San Diego

Nanoscale patterning is one of the key interests in the semiconductor industry. For nanoscale patterning applications, inherently selective deposition methods (no passivants) are being studied to use in conjunction with double patterning techniques as shown in Fig. 1. This chemically based patterning is needed in backend fabrication when multiple metals and low k dielectric layers such as SiCOH (hydrophobic porous carbonized silica) are employed. For selective deposition in backend fabrication, water-free deposition is desirable since it induces higher selectivity [1] and prevents damage of metals and SiCOH.

Previously, the inherent selective CVD of $TiO_2$ was studied on Si, $SiO_2$ and SiCOH. Around 17 nm and 40 nm of $TiO_2$were deposited on Si and $SiO_2$, respectively, with less than 0.1 nm on SiCOH. However, due to nano-crystallization, the films had rough surfaces (Fig. 2.) which has to be reduced for nanoscale patterning applications. By forming nanolaminate structures of two different oxides, this crystallization can be surpressed[2,3]. In the present study, sequential pulsed CVD at 300˚C sample temperature using titanium isopropoxide and hafnium tert-butoxide to form an amorphous $HfO_2$/$TiO_2$ nanolaminate film was studied.

Due to inherent (passivation-free) surface reactivity difference of each precursor, $HfO_2$/$TiO_2$ nanolaminate films were selectively deposited on Si and $SiO_2$ in preference to SiCOH. By controlling $HfO_2$ and $TiO_2$ sublayer thickness and the Hf:Ti ratio, amorphous and selective deposition of the $HfO_2$/$TiO_2$ nanolaminate film could be achieved simultaneously. Thick films were selective deposited: ~20 nm of amorphous $HfO_2$/$TiO_2$ nanolaminate was selectively deposited on Si and $SiO_2$ in preference to SiCOH (<0.1 nm) with an RMS roughness <1 nm as shown in Fig. 3.

To check for nanoscale patterning application, selective deposition of the $HfO_2/TiO_2$ nanolaminate film was tested on a Cu/SiCOH nm scale patterned sample. TEM imaging (Fig. 4) demonstrates that the $HfO_2/TiO_2$ nanolaminate film can be selectively deposited only on Cu surface even for nanometer scale features.

This study demonstrated high selective oxide deposition by inherent reactivity difference of precursor mediated chemisorption on the nm scale. For nanolaminate structures with 1-2 nm sublayer thickness, crystallization can be suppressed which make this process suitable for patterning.

**AS3-10 Optimization of Substrate-Selective Atomic Layer Deposition of Zirconia on Different Forms of Copper Using Ethanol as Precursor Reactant and Surface Pre-Treatment***, Soumya Saha,* University of Illinois at Chicago*; N. Anderson,* Intel Corporation*; G. Jursich, C. Takoudis,* University of Illinois at Chicago

Copper is currently the material of choice for making interconnects in semiconductor devices and zirconia, having a high dielectric constant, could replace silicon dioxide as the gate dielectric material in the near future. Atomic layer deposition (ALD) has emerged as the ‘bottom-up’ technique due to its capability of depositing uniform ultra-thin films and potential for area selectivity. In this study, zirconium dioxide was selectively deposited on silicon and not on copper for at least up to 100 ALD cycles using tris(dimethylamino)cyclopentadienyl zirconium as the zirconium precursor and ethanol as the precursor reactant in a custom made ALD system (Patent #10214817). Typically, copper is electroplated and then chemical mechanical polished. Here, both electroplated (EP) and electroplated copper with chemical mechanical polishing (CMP) were used for this study and subtle difference in surface oxides on EP and CMP copper and the choice of reactant influenced selectivity of deposition. Under suitable ALD processing deposition was inherently selective on EP copper and could be achieved on CMP copper only after optimizing the deposition process parameters. $ZrO_2$, selectively deposited via ALD, was characterized using spectral ellipsometry, X-ray photoelectron spectroscopy and extended X-ray absorption fine structure spectroscopy.

## Area Selective ALD
## Room On Demand - Session AS4
## Area Selective ALD Poster Session

**AS4-1 Effect of Surface Cleaning Efficacy on Vapor-Phase Cleaning of Cu and Co Using Anhydrous $N_2H_4$***, Su Min Hwang, J. Kim, D. Le, R. Gummadavelly, Y. Jung, J. Veyan,* University of Texas at Dallas, USA*; D. Alvarez, J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas, USA

As the critical dimension of current Copper (Cu) metal line shrinks below 5 nm, the resistivity of Cu is expected to increase drastically, due to electron scattering at the sidewall and grain boundaries.[1] In addition, the high-resistivity liner and diffusion barrier, currently required in the copper interconnects, attribute to the decrease of effective width of Cu. To circumvent this issue, the study of alternative materials to Cu have been reported. Among the various metals, Cobalt (Co) has been proposed as a potential material with comparable resistivity below 7 nm thickness.[2] Several processes on ALD of Co have been reported requiring an additional reduction step to obtain metallic Co. Therefore, it is imperative to explore reducing agents capable of reducing the oxide on Co at low temperatures. Recently, hydrazine ($N_2H_4$) has been reported as the reducing agent of the Cu oxide due to its higher reduction capability.[3] Inspired by hydrazine’s unique characteristics, we explore the feasibility of vapor-phase reduction of Co oxide using $N_2H_4$ to achieve an ideal metallic Co film in an ALD environment. Additionally, a detailed reduction mechanism of the Co oxide by comparing with Cu oxide will be studied using *in-situ* surface analysis. In this study, we have demonstrated the effect of vapor-phase cleaning on Cu and Co using anhydrous $N_2H_4$ with its high reduction capability to remove surface contaminants and metal oxide. The Cu film with 1.5 µm thickness and the Co film with 200 nm thickness were deposited on a silicon substrate using electroplating and sputtering, respectively. The preparedCu and Co films were treated with ALD-like multiple exposures of $N_2H_4$ in the temperature range of 100 – 400 °C. Each cycle consisted of 0.5 s $N_2H_4$ exposure and 120 s Ar purge. The XPS analysis of the Cu samples treated at 200 °C show a significant amount of copper oxide was reduced to metallic copper with an approximate thickness of 1 nm. Meanwhile, the Co samples show the cleaning efficacy at above 350 °C due to the relative stability of the cobalt oxide. In addition, *in-situ* reflection absorption infrared spectroscopy (RAIRS) was employed to elucidate the individual surface chemistry of Cu and Co films during the $N_2H_4$ exposure step. The detailed experimental results will be presented.

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[1] P. Kapur, et al., IEEE Trans. Electron Devices **49**, 590 (2002).

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

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

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