Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+EM+PS+TF-TuM

Area Selective Processing and Patterning

Moderators: Prof. Dr. Greg Parsons, North Carolina State University, **Dr. Silvia Armini**, IMEC, Belgium

8:00am **AP+EL+EM+PS+TF-TuM-1 ASCEND: A Novel Solution-Based Method To Control Deposit Composition and Placement**, *Jevalyne Vienes,* ***Amy Walker,*** University of Texas at Dallas

We introduce a novel selective deposition process called ASCEND, or "Additive and Surface Control of Electroless Nanostructure Deposition." ASCEND integrates mechanistically-informed and well-controlled extensions of electroless deposition (ELD) and chemical bath deposition (CBD). It uses hybrid ELD-CBD conditions and patterned surfaces to deposit strongly adherent metallic and metal chalcogenide films and nanowires. It is inexpensive, easily scaled, and compatible with technologically relevant substrates. We illustrate ASCEND using Cu and CuS deposition. First, we employ ethanolamine additives in Cu ELD using dimethylamine borane (DMAB) on –OH and $–CH_3$ terminated alkanethiolate self-assembled monolayers (SAMs) either to deposit nanowires or perform area-selective deposition. Using monoethanolamine or triethanolamine copper nanowires are formed at the junction of patterned –OH/$–CH_3$ terminated SAMs. In contrast using diethanolamine, area selective deposition is observed in the $–CH_3$ terminated SAM area. Using TOF SIMS data we show that monoethanolamine and triethanolamine adsorb vertically (or at an angle) with the amine group interacting with the $–CH_3$ terminated SAM and leaving the hydroxyl groups free to interact with the bath components. This causes repulsion of the DMAB reducing agent, hindering deposition on the $–CH_3$ terminated SAM areas leading to nanowire formation. In contrast, diethanolamine adsorbs flat on $–CH_3$ terminated SAMs and no nanowire formation is observed; rather area-selective deposition occurs.

In the second experiment we control the deposit composition in Cu ELD using thiourea, which is a common bath additive, on -OH, -COOH and $–CH_3$terminated SAMs. At < 10^{-2} M thiourea, Cu films are deposited on all substrates. At ≥ 10^{-2} M the deposited layers are copper sulfides. At pH 5 and pH 9, the film is composed of CuS for all functionalized SAMs studied, while at pH 12 the deposit is Cu_2S. We attribute this to the role of thiourea in the bath. At low concentrations, thiourea acts as a complexing and reducing agent, while at high concentrations (> 10^{-2} M) the dominant reaction is thiourea hydrolysis leading to the formation of copper sulfides. Finally, exploiting this understanding we demonstrate a simple method to deposit layered Cu/Cu_xS and CuS nanowires on patterned SAM substrates by changing the TU concentration in the bath.

8:15am **AP+EL+EM+PS+TF-TuM-2 Using Acetylacetates to Control Chemical Reactivity and Physical Properties of Surfaces**, ***Andrew Teplyakov,*** University of Delaware

Over the last few years, the applications of various acetyl acetates in tuning both chemical reactivity of surfaces in deposition and etching processes and physical properties of the interfaces and thin films have received a substantial attention both from fundamental perspective and from applications point of view. This presentation will analyze the chemistry of several acetylacetates, including the ligands formed on surfaces by acetylacetone (acacH), hexafluoroacetylacetone (hfacH) and 1,1,1-trifluoroacetylacetone (tfacH) and the implications of this chemistry in area-selective atomic layer deposition (AS-ALD), atomic layer etching (ALE), and tuning optoelectronic properties of oxide surfaces and thin films. The effects of the gas-phase keto-enol equilibrium and the acid/base properties of oxide surfaces on the adsorption mechanisms will be discussed. The applications of this knowledge to design non-growth and growth surfaces for ALD and to propose new chemistries for ALE of 2D materials will be demonstrated.

8:30am **AP+EL+EM+PS+TF-TuM-3 Atomic Layer Etching for Advanced Logic Devices**, ***Masanaga Fukasawa,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The dimensions of advanced logic devices require atomic-level control of variability, and atomic-layer etching (ALE) is a promising technique to meet this requirement. By separating adsorption and desorption, ALE improves controllability compared with conventional RIE. Currently, however, the long process time—leading to increased manufacturing cost—remains a major challenge, and thus industrial adoption has been limited. Nevertheless, in next-generation highly scaled 3D transistors such as CFETs, further improvements in etch selectivity, mitigation of pattern loading, and reduction of etch-induced damage are required. As a result, the importance of ALE is expected to increase [1].

To further improve etch selectivity, we have developed a technique that integrates area-selective deposition (ASD) and ALE within a single etching chamber to achieve ultra-high etch selectivity [2]. In atomic-scale processes such as ALD and ALE, understanding surface reactions and process performance at the atomic level enables more precise process design through the combination of individual reaction steps. Moreover, this approach is beginning to be adopted not only for ASD + ALE but also for ASD + RIE [3] in various process modules. In particular, with High-NA EUV lithography reducing resist thicknesses to below 30 nm, extremely high etch selectivity becomes even more critical. Thus, integration schemes that combine ASD with RIE/ALE will play an increasingly important role.

Regarding low-damage processing, although several studies have reported blanket-level evaluations, examples that demonstrate practical-level performance have been limited. In this work, we applied ALE or RIE to the bottom-break step of contact hole etching and compared the resulting electrical characteristics of contact chains. The results clearly show that ALE provides superior performance [4].

ALE delivers the controllability, reproducibility, and integrability required for next-generation semiconductor technologies, and elevates semiconductor fabrication to a new level of precision. I believe ALE will become increasingly essential in advanced logic device manufacturing.

Acknowledgement: This paper is based on results obtained from the project, "Research and Development Project of the Enhanced Infrastructures for Post-5G Information and Communication Systems" (JPNP20017), subsidized by New Energy and Industrial Technology Development Organization (NEDO).

[1] M Honda *et al., J. Phys. D: Appl. Phys*. **50**, 234002 (2017). [2] M. Fukasawa *et al., JJAP.* **64,** 06SP17 (2025).

[3] M. Matsui *et al., JVST A* **41**, 063002 (2023). [4] A. Hirata *et al., Proc. of IEEE IITC (*2026), San Jose, accepted for oral presentation.

9:00am **AP+EL+EM+PS+TF-TuM-5 Band Practice: Tuning Gold's Workfunction Through NHC d-Band Interactions**, ***Sean Barry,*** Carleton University, Canada*; Wai Tung Shiu, Paul Ragogna,* Western University, Canada

N-heterocyclic carbenes (NHCs) have emerged as robust small-molecule inhibitors (SMIs) for modifying metal surfaces, yet a quantitative understanding of their influence on surface electronic structure remains limited. Here, we investigate the modulation of the d-band center of a gold surface by NHC adsorption using a combination of solution- and vapour-phase deposition. Four structurally distinct NHCs were deposited on Au substrates, and the resulting interfaces were characterized using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

All NHCs formed stable monolayers on Au, with surface coverages that depended on both molecular structure and deposition method, ranging from 1.88 to 3.56 NHC/nm^2. UPS measurements revealed significant reductions in the Au work function (up to ~1.2 eV), with vapour-deposited films exhibiting larger shifts, consistent with differences in interfacial structure and electron redistribution. Analysis of the valence band spectra shows a systematic lowering of the Au d-band center upon NHC adsorption, indicating increased filling of antibonding states and weakened adsorbate–metal interactions.

Three primary factors governing d-band modulation were molecular orientation and the formation of $Au(NHC)_2$ adatom complexes, which lead to enhanced electron donation. Surface coverage plays a critical role, with higher coverages producing stronger modulation due to increased adsorbate–metal interactions. Finally, ligand electronics, particularly backbone substitution, influence the NHC's σ-donating ability and thus the extent of electronic perturbation at the interface.

This presentation will discuss the structure-function relationships of NHC substitution and coverage as well as absorption interactions.

9:15am **AP+EL+EM+PS+TF-TuM-6 Inhibition of SiO_2 by plasma treatments for bottom-up gap-fill applications**, ***Aurelia Trevisan,*** *Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

As the features in electronic devices become smaller, top-down processes based on lithography need eventually to be complemented by bottom-up processes such area selective atomic layer deposition (AS-ALD). Although

ALD allows for conformal deposition on 3D features, it is challenging to fill high aspect ratio (AR) trenches without the formation of defects such as voids and seams in the middle. To obtain a defectless bottom-up gap-fill of a trench by ALD, the growth per cycle (GPC) of the employed ALD process should be lower at the top of the trenches than at the bottom. Different approaches that result in a decreased GPC on the top of AR trenches for seamless gap-fill have been studied employing molecular inhibition species[1] and NH_3 plasma pre-treatments.[2]

In this work, we investigated the mechanisms of inhibition of SiO_2 by NH_3, N_2/H_2 and SF_6/H_2 plasma exposures aiming at the application of such plasma pre-treatment for achieving gap-fill with SiO_2. We exposed the SiO_2 surface to NH_3, N_2/H_2 and SF_6/H_2 plasma at different conditions and we studied the surface chemistry by reflection-absorption infrared spectroscopy (RAIRS). For a NH_3 plasma exposure, we found that the substitution of the OH groups with NH_2 groups is almost complete[3] at low NH_3 pressure from the comparison of the areas of the OH peak (~3740 cm^{-1}) in the RAIRS spectra acquired after the plasma exposures at different NH_3 pressures. Next, to investigate the inhibition of the SiO_2 surface by plasma, RAIRS spectra were also obtained after dosing the Si precursor, bis(diethylamino)silane (BDEAS), with and without the plasma treatment step. From the IR spectra, we found that the amount of adsorbed BDEAS molecules on SiO_2 pre-treated with NH_3 plasma (60s, 0.01 mbar) is reduced by ~82%.

A NH_3 plasma pre-treatment was added before the dose of the precursor to every cycle of the SiO_2 PE-ALD process. The effect of the NH_3 plasma pre-treatment on the growth was investigated by conducting spectroscopic ellipsometry (SE) after every cycle. When the NH_3 plasma pre-treatment was added, a 53% reduction of the GPC was obtained. We expect this reduction to be enough to achieve gap-fill of high AR trenches, which will be studied by cross-sectional transmission electron microscopy.

References

[1] C. T. Nguyen *et al., Nature Communications* **13**, 7597 (2022)

[2] Y. Choi *et al.*, *Scientific Reports* **12**, 15756 (2022)

[3] L. T. Zhuravlev, *Colloids and Surfaces A: Physiochemical and Engineering Aspects* **173**, 1-38 (2000)

9:30am **AP+EL+EM+PS+TF-TuM-7 Precursor Isomerization-Enabled Etching Amplification: A Novel Route to Area Selective Deposition of SiOC Films**, ***Xiaocheng Huang**, Junjie Zhao,* Zhejiang University, China

Self-aligned patterning via area selective deposition (ASD) is a promising approach to mitigate overlay variations challenges in photolithography for advanced nanomanufacturing. However, it remains difficult to achieve area selective deposition when the adsorption and/or film growth on the target non-growth surface (NGS) exceeds that on the target growth surface (GS). We developed an etching amplification strategy based on precursor isomerization for selective deposition of SiOC when adsorption and/or film growth was higher on the target NGS than on the target GS. *In-situ* DRIFTS demonstrated that V_3D_3 cyclosiloxane undergoes ring-opening on CoO_x surfaces. This ring-opening reaction significantly enhances the etching rate under O_2/Ar plasma by 243% compared to the pristine pV_3D_3, as confirmed by *in-situ* QCM measurements. *In-situ* QCM during ASD cycles showed higher mass gain on CoO_x than on SiO_2 during V_3D_3 deposition steps; however, the subsequent etching step completely removed the adsorbed species from the NGS due to etching amplification. By integrating deposition and etching processes, we achieved selective deposition of a ca. 18.36 nm thick SiOC film on pre-patterned Co/SiO_2 substrates with nearly 100% selectivity. This work sheds light upon etching amplification by precursor isomerization for developing highly selective ASD processes.

9:45am **AP+EL+EM+PS+TF-TuM-8 A Novel Hybrid Approach to Area-Selective Deposition: Combining Two Strategies for Blocking Growth**, *Jay Swarup, James Jensen, Gokul Rajagopal, **James Engstrom**,* Cornell University

Area-selective atomic layer deposition (AS-ALD) has emerged as a promising bottom-up nanofabrication strategy for next-generation semiconductor manufacturing, where continued device scaling makes conventional lithographic patterning increasingly difficult and costly. Selectivity can be achieved by passivating non-growth surfaces (NGS) with blocking molecules while permitting growth on designated growth surfaces (GS), and it depends critically on precursor chemistry, blocking molecule identity and application method, and reactor temperature. Here we systematically investigate two blocking strategies for AS-ALD of Al_2O_3 targeting selective growth on Cu (GS) with suppression on SiO_2 (NGS) using BDMADA-Al, a bulky, non-pyrophoric precursor [1]. We employ *in situ* real time quartz crystal microbalance (QCM) techniques, coupled with selected *ex situ* techniques including X-ray photoelectron spectroscopy (XPS).The first strategy employs sequential dosing of a small molecule, while the second strategy introduces a co-adsorbate dosed simultaneously with the precursor to enable competitive adsorption at NGS reactive sites. In the first strategy, dimethylamido trimethylsilane (DMATMS) was applied repetitively in an ABC-type cycle (T = 285 °C), which produced modest blocking efficacy, where detectable growth from QCM could be delayed for the first ~ 20 cycles, while Al is clearly observed with XPS after 40 cycles.In the second strategy we also employ an ABC-type cycle, but also introduce a co-adsorbate dosed simultaneously with BDMADA-Al at T = 120 °C.We examined six different co-adsorbates, all possessing reactive functional groups, which revealed stark differences in blocking efficacy depending on the co-adsorbate used.Three co-adsorbates did not enhance blocking but, rather, produced linear (with exposure time) CVD-like growth during the combined precursor/co-adsorbate pulse.In contrast, three co-adsorbates yielded *complete blocking* of growth on SiO_2 for at least 40 cycles of ALD, confirmed by both QCM and XPS.In order to verify the operative mechanism of competitive adsorption we varied both the partial pressure of the co-adsorbate and the reactor temperature.We found that by either decreasing the partial pressure of the co-adsorbate, or increasing the temperature led to less effective blocking of growth, confirming the mechanism based on competitive adsorption.These results demonstrate that an approach that combines two strategies can produce synergy and a more effective method to enable area selective deposition.

[1]J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You and J. R. Engstrom, J. Vac. Sci. Technol. A **43**, 022404 (2025).

11:00am **AP+EL+EM+PS+TF-TuM-13 Probing Reactivity at Heterointerfacial Sites Using Area Selective Atomic Layer Deposition**, *Shani Monadeev, **Oz M. Gazit**, Alexander Stook,* Technion Israel Institute of Technology, Israel

Background

Heterointerfaces are a sub-class of defects arising from atomic mismatches across material boundaries. These coordinatively unsaturated sites modulate the electronic and geometric structure of catalysts to facilitate specific reactive adsorption, activation, and transformation of reactant molecules.[1] In electronic devices the critical heterointerfaces are “buried” between the layers,[2] whereas for catalysts, the reaction performance can depend on both the buried interfaces (i.e. metal support interactions) and on the exposed heterointerfacial (defect) sites, interacting with substrate and product molecules, see **Scheme 1**.

Results and discussion

In the current work, we use a bottom-up area selective atomic layer deposition (AS-ALD) to form supported thin layer raft-like oxides. To facilitate the AS geometry, we developed a new approach, which uses NaCl nanocrystals as masking domains during the ALD process. This unique approach allows us to apply this methodology onto silicon wafers and on different surface area particulate silica support materials. The HRSEM-EDS (Energy Dispersive Spectroscopy) mapping in **Figure 1** shows an example of a well-defined multilayer structure, formed following the sequential deposition of TiO_2 (≈20 nm) and subsequently Al_2O_3 (≈20 nm) layers onto an NaCl-mask before and after mask removal. Leveraging on the strength of AS-ALD we study the structure, binding energy, strain and more of the exposed heterointerface, aiming to decuple those from the exposed basal plan and bulk effects. We compare our AS-ALD materials to materials obtained using a top-down deposition of thin nanosheets of layer double hydroxides. All materials are extensively characterized using XPS, DRIFT-IR, HRSEM and HRTEM, grazing angle-WAXS and probe molecules TPD-MS. The functionality of the heterointerfacial sites is tested using Aldol type condensation reactions for the conversion of biomass derived platform molecules as a target and probe reaction.

References

(1)Xie, C., et al., ACS Catal. 2020, 10 (19).

(2)Christensen, D. V., et al., APL Materials 2018, 7 (1), 013101.

11:15am **AP+EL+EM+PS+TF-TuM-14 Area-selective Atomic Layer Deposition of Al2O3 on SiNx with Aminosilane-Functionalized SiO2 as the Nongrowth Surface**, ***Andrew Kaye**,* Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Ronald Pearlstein, Haripin Chandra, Agnes Derecskei,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

SiO_2 and SiN_x are two of the most extensively used dielectric materials in semiconductor manufacturing. Previously, we showed that area-selective ALD of Al_2O_3 can be achieved on SiN_x by passivating the SiO_2 surface with

aminosilanes. Using *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy (see Figure 1), we will show that the aminosilanes react with both the SiO_2 and SiN_x surfaces, but the coverage of aminosilanes on the SiN_x surface is incomplete, which does not prevent ALD of Al_2O_3 from dimethylaluminum isopropoxide (DMAI) and H_2O, but simply introduces a nucleation delay of 5-10 cycles. However, selective growth of Al_2O_3 on SiN_x was limited to ~1 nm at which point DMAI started to react with the SiO_2 surface to nucleate film growth.

Based on these initial studies, our hypothesis was that there are residual Si–OH groups that remain on the SiO_2 surface react with DMAI to initiate growth of Al_2O_3. We have also shown that DMAI likely coordinates with Si–O–Si groups on aminosilane-functionalized SiO_2 films, which also leads to nucleation; therefore, simply reducing the surface Si–OH group density is inadequate. To extend the nucleation delay on SiO_2, we created a set of plasma-deposited SiO_2 surfaces with a controlled density of surface Si–OH groups by first preheating from the deposition temperature of 150 °C up to 500 °C, and then by cooling the substrate to a lower temperature prior to ALD of Al_2O_3. We used aminosilanes with different size head groups to study the uptake of aminosilanes and the steric blocking effects of both Si–OH and Si–O–Si sites to block Al_2O_3 ALD. The headgroup size did not significantly impact the initial uptake of aminosilanes with the same size leaving groups (see Figure 2). Using *in situ* ellipsometry, we show that aminosilanes with larger head groups resulted in more selective growth on SiN_x over SiO_2. Next, we showed that increasing the aminosilane dose increased the nucleation delay of Al_2O_3 ALD on both SiO_2 and SiN_x surfaces due to increased coverage, but selectivity did not improve significantly. Finally, we show that using a two-step aminosilane passivation scheme with sub-saturation doses of a large aminosilane and then a small aminosilane resulted in >3 nm of selective Al_2O_3 ALD on SiN_x over SiO_2 surfaces (see Figure 3).

11:30am **AP+EL+EM+PS+TF-TuM-15 Beyond Two-Color Selectivity: Area Selective Deposition on Multi-Oxide Surfaces Using Small Molecules Inhibitors***, **Benjamin Sanhueza,** Marc J. M. Merkx, Wilhelmus M. M. Kessels,* Eindhoven University of Technology, Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J.M. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) using small molecule inhibitors (SMIs) emerges as a promising bottom-up alternative, enabling selective deposition on growth areas (GAs) while inhibiting the non-growth areas (NGAs). Although ASD has shown strong potential, most studies are limited to two-surface-selectivity, which does not capture the multi-material complexity of modern semiconductor devices.[1]. In this context, we investigate the selectivity of SiO_2 ASD in a multi-oxide system by evaluating the role of different SMIs and their impact on inhibition selectivity, with relevance on 3D memory [2] and 3D logic devices.[3]

Here, we employ a previously developed SiO_2 ASD process on Al_2O_3 and SiO_2 surfaces,[4] using the bis(diethylamino)silane (BDEAS) precursor, H_2 and O_2 plasma as co-reactants, and different SMIs. Building on this process, we investigate multi-surface selectivity by introducing ZrO_2 as an additional third oxide surface.

Among the SMIs investigated, acetylacetone (Hacac) is presented as a representative case. *In situ* reflection–absorption infrared spectroscopy (RAIRS) shows that Hacac reacts with ZrO_2, achieving surface saturation and up to 96% blocking of a single BDEAS dose, which is comparable to that observed on Al_2O_3 as an NGA. Preliminary results further indicate that the H_2 plasma pre-treatment increases the density of isolated and vicinal –OH groups, enhancing Hacac coverage and improving blocking up to 99.5%, demonstrating the strong influence of this plasma pre-treatment on the ZrO_2 surface.

In situ ellipsometry measurements show that ZrO_2 acts as an effective NGA, exhibiting a nucleation delay of up to 28 cycles (~2.6 nm of selective SiO_2 deposition). Remarkably, similar selectivity is achieved on both Al_2O_3 and ZrO_2 surfaces, indicating consistent inhibition behavior across different oxides.[1], [5]

In addition to the results of this case study, it will be discussed that the choice of SMIs can tune inhibition behavior enabling different growth across surfaces. In this way, the loss of selectivity can be preferentially initiated on one NGA prior to another through SMI selection, enabling controlled thickness variations across different materials.

References

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[4]: Yu et al., *Appl. Surf. Sci.* 665 (2024) 160141

[5]: Thelven et al., *Adv. Mater. Technol.* 10 (2025), e00284.

11:45am **AP+EL+EM+PS+TF-TuM-16 Surface Hydroxyl Topology and Relative Orientation Effects on Surface-Inhibitor Reactivity: Revisiting Chemical Passivation in Alumina and Zirconia.***, Lucas Lodeiro, Nicolás Rozas-Castro,* Universidad Tecnica Federico Santa Maria, Chile*; Dennis Hausmann, Rachel Nye de Castro,* Lam Research Corporation*; Adriaan Mackus,* Eindhoven University of Technology, Netherlands*; **Tania Sandoval,*** Universidad Tecnica Federico Santa Maria, Chile

Hydroxylated metal oxide surfaces are paramount for catalysis and thin–film processing. In this context the reduction of surface reactivity via molecular inhibitors or chemical passivation is a common and necessary practice. Small–molecule inhibitors (SMIs) such as acetylacetone (Hacac) and acetic acid (HAc) are widely employed to inhibit growth by reactive site consumption on hydroxylated oxides.[1] Despite their ubiquitousness, the influence of **surface site configuration** on inhibitor reactivity remains unexplored.

Experimental evidence that chemically distinct hydroxyl motifs exhibit different reactivities toward SMIs is available.[2] In this work, we revisit the chemical passivation of hydroxylated alumina and zirconia by SMIs, with emphasis on the role of surface site configuration, defined as a combination of Local Topology and Relative Orientation of hydroxyl groups on metal oxide surfaces. Rather than treating hydroxylated sites as a whole entity, we examine how geometrically and electronically distinct surface motifs modulate inhibitor binding modes and reactivity.

Considering that systematic exploration of all possible site configurations rapidly becomes challenging due to the large chemical space, we further investigate whether simple surface descriptors, derived from local electronic structure and geometry, can provide predictive insight into surface reactivity toward SMIs. Our goal is to identify descriptor trends (e.g., charge distribution, coordination, or accessibility metrics) that correlate with inhibitor adsorption behavior, enabling informed prioritization of surface motifs prior to exhaustive site screening.

By linking surface site configuration, inhibitor-surface reactivity and descriptor–based analysis, this work aims to understand the nuances in the chemical passivation of metal oxide surfaces, and provides guidance to design descriptor–informed screening strategies.

[1] Chem. Mater. 2020, 32, 3335–3345

[2] J. Phys. Chem. C, 2022, 126, 4845–4853

12:00pm **AP+EL+EM+PS+TF-TuM-17 Can pFA Invert Selectivity? The Chemistry of TiO_2 Nucleation on Chlorinated and Aminated Si(111) Surfaces During Thermal Atomic Layer Deposition***, **Tyler Parke,** Andrew Teplyakov,* University of Delaware

Recently, the near-atomic level precision offered by atomic layer deposition (ALD) has been exploited by developing area-selective schemes which can be used to fabricate complex three-dimensional nanostructures, such as modification of a substrate's surface functionality to induce a "selectivity inversion" between growth surfaces (GS) and non-growth surfaces (NGS). This is a newly developing technique, which has only been demonstrated thus far with few vapor-phase treatments, and which requires a molecular level understanding of the chemistry between surface and modifying reactant, as well as between modified surface and precursor. Here, single-crystal Si(111) surfaces terminated with hydrogen [H-Si(111)] or chlorine [Cl-Si(111)] monolayers, which are typically NGS's in thermal TiO_2 processes, are proposed as potential substrates to modify with a basic amine, para-fluoroaniline (pFA), and invert their selectivity. Amination with pFA is demonstrated to selectively modify the H-Si(111). Thermal TiO_2 ALD is subsequently attempted to test the aminated surface's capability as a GS or NGS. The fundamental chemistry of the interaction between the pFA and either surface, as well as between the aminated surface and ALD precursors $TiCl_4$ and tetrakis(dimethylamido)titanium (TDMAT), are probed with a combination of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), density functional theory (DFT), and time of flight secondary ion mass spectrometry (ToF-SIMS) in order to determine the structure of the aminated surface and understand its effect on reactivity under ALD conditions.

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