Atomic Scale Processing Mini-Symposium
Room 206 A W - Session AP+EM+PS+TF-FrM

Area Selective Processing and Patterning

Moderators: Steven M. George, University of Colorado at Boulder, **Angelique Raley**, TEL Technology Center, America, LLC

8:15am **AP+EM+PS+TF-FrM-1 Exploring Intermolecular Interactions of an Acetylacetone Variant as Small Molecule Inhibitor for Area-Selective ALD**, ***Eric Ha Kit Wong***, *Marc J. M. Merkx, Joost F. W. Maas,* Eindhoven University of Technology, The Netherlands*; Ilker Tezsevin,* Eindhoven University of Technology, Netherlands*; Wilhelmus M. M. Kessels,* Eindhoven University of Technology, The Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J. M. Mackus,* Eindhoven University of Technology, The Netherlands

Self-assembled monolayer (SAMs) and small molecule inhibitors (SMIs) are two types of inhibitors for area-selective atomic layer deposition (AS-ALD). One critical requirement for inhibitors is to form densely packed adsorbate layers on the non-growth area. SMIs can be delivered in the vapor phase, which makes them compatible with existing industrial processes. However, the random sequential adsorption of SMIs tend to leave gaps in between the adsorbates (*1*). Intermolecular interactions could improve SMI packing and coverage, potentially leading to a higher selectivity.

π-π interaction is an important class of intermolecular interactions that has been employed in different fields (*2*). To exploit π–π interactions in SMIs, one can introduce aromatic backbones to the molecule. In this work, 3-phenyl-2,4-pentanedione (Hppa (*3*)) is used as the structural variant of acetylacetone (Hacac) for inhibiting ALD on Al_2O_3 as the non-growth area over the growth area of SiO_2.

Using in–situ reflection–absorption infrared spectroscopy, we examined saturation behaviour, precursor blocking, and thermal desorption of Hppa. The results indicate that Hppa has similar adsorption behaviour as compared to Hacac, in terms of saturation dosages and bonding configurations. Still, various important differences are found: Firstly, the Hppa adsorbates exhibit a transition from a flat-lying configuration at low coverage, to a standing-up configuration at high coverage, suggested by the emergence of the sp^2 ν(CH) peak. This indicates that the adsorbates are in orientations that could contribute to π-π interaction. Secondly, the results of blocking tests suggested that Hppa adsorbates are not displaced from the surface by bis(diethylamino)silane (BDEAS) precursor molecules, in contrast to the Hacac case in which ca. 5% of acac adsorbates are removed from the surface by BDEAS. Thirdly, Hppa adsorbates does not show thermal desorption at 150 °C for 10 hours. Instead, the increase in peak area suggest that the adsorbates might undergo rearrangement to other orientations. In summary, our results suggest that the Hppa can be an effective SMI for AS-ALD.

Reference

1. J. Li *et al.*, *J. Vac. Sci. Technol. A*. **40**, 062409 (2022).
2. R. Thakuria, N. K. Nath, B. K. Saha, *Crystal Growth & Design*. **19**, 523–528 (2019).
3. O. A. Serra, E. J. Nassar, P. S. Calefi, I. L. V. Rosa, *Journal of Alloys and Compounds*. **275–277**, 838–840 (1998).

8:30am **AP+EM+PS+TF-FrM-2 the Influence of Intermolecular Interaction on the Packing of Small Molecule Inhibitors: A Simulation Study**, ***Joost Maas***, *Marc Merkx,* Eindhoven University of Technology, Netherlands*; Tania Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adrie Mackus,* Eindhoven University of Technology, Netherlands

In recent years, using small molecule inhibitors (SMIs) has become one of the main approaches to achieve area-selective atomic layer deposition (AS-ALD). The main challenge for area-selective deposition (ASD) using SMIs is to obtain a high packing of inhibitor molecules on the surface. Due to the vapor phase dosing, molecules arrive one-by-one at random locations, which leaves gaps in between the inhibitors where potentially a precursor can adsorb, causing loss of selectivity.[1]

In this work we explore the use of attractive intermolecular interactions for achieving higher packing of SMIs via simulations. When employing small molecules, it is expected that van der Waals interactions are too weak to contribute to packing. Consequently, one of the main questions of this work is how strong the interaction has to be to facilitate ordering of molecules on the surface. In addition, the synergy of intermolecular interaction and diffusion of SMIs over the surface is investigated.

The simulation method used for studying the packing of molecules with intermolecular interaction and diffusion is an augmented random sequential adsorption (RSA) model.[1] During every loop of the RSA model, either adsorption or diffusion takes place, based on the adsorption and diffusion rates. The intermolecular interaction energy is implemented in the form of a Metropolis-Hastings algorithm.[2] In the initial work, the molecule is a simple disk on a hexagonal grid with periodic boundary conditions, considering nearest neighboring blocking.

It was found that the coverage of the SMI improves significantly for low diffusion barriers and attractive intermolecular interaction. For interactions energies stronger than approximately -0.15 eV, the formation of domains of higher density on the surface is observed. The results suggest that coverage can be improved significantly by selecting SMIs with sufficient interaction energy and a low diffusion barrier.

1. J. Li; et. al., *JVST A* **2022**, 40 (6), 062409
2. M. Kalos; et. al., *The Annals of Statistics* **1986**, 22 (4), 1701-1762

8:45am **AP+EM+PS+TF-FrM-3 Tuning Surface Reactivity by Small Molecule Modifiers in Area-Selective ALD: Small Molecule Inhibitors (SMI) vs. Small Molecule Promoters (SMP)**, ***Andrew Teplyakov***, University of Delaware

In area-selective deposition, selectivity of surfaces could be manipulated to either suppress or promote surface reactivity with respect to the target reactants. Using model ALD processes with TiO_2 (TDMAT/water) or Al_2O_3 (TMA/water), the deposition onto semiconductor surfaces modified with small fluorine-containing molecules is analyzed by spectroscopic and microscopic techniques, including depth profiling with ToF-SIMS, supplemented by computational DFT modeling. The fluorinated functional groups are designed for easy spectroscopic characterization to analyze the potential AS-ALD schemes on silicon, as well as on oxide materials, including TiO_2, MgO, and Al_2O_3. The initial deposition steps are analyzed by comparing the behavior of modified surfaces with that of pristine substrates, and the distribution of the fluorine and fluorine-containing fragments within the ALD-deposited layers is followed by ToF-SIMS depth profiling once these F-containing functionalities are buried under the overgrown layers. This approach allows for identification of the deposition processes for both small molecule inhibitors (SMIs) and small molecule promoters (SMPs).

9:00am **AP+EM+PS+TF-FrM-4 Topographically Selective Atomic Layer Etching of HfO_2 and ZrO_2 Using NbF_5 and $TiCl_4$**, ***Boyun Choi***, *Getasew Zewdie, Hyeyoung Shin, Nari Jeon,* Chungnam National University, Republic of Korea

As transistor dimensions continue to shrink, conventional SiO_2 gate dielectrics no longer provide adequate capacitance or leakage control, leading to the widespread adoption of high-k oxides such as HfO_2 and ZrO_2. Yet, achieving atomic-level patterning of these oxides remains a key challenge for advanced device integration. In this study, we investigate their thermal atomic layer etching (ALE) behaviors using NbF_5 and $TiCl_4$ as representative halide reactants. A pronounced contrast emerges: HfO_2 undergoes smooth, self-limiting etching cycles, whereas ZrO_2 exhibits surface roughening and substantial chlorine incorporation. Density functional theory calculations clarify this difference by showing that $TiCl_4$ reacts more aggressively with ZrO_2 surface species, destabilizing the surface and degrading etch quality. Extending ALE to nanohole structures with a diameter of 150 nm and a depth of 2000 nm, we further observe topographically selective removal of HfO_2. This selectivity is linked to microstructural factors such as crystallinity, indicating that not only chemical reactivity but also structural variations critically influence ALE outcomes. Taken together, these results establish a mechanistic framework for understanding how reactant chemistry and microstructure jointly govern the etching of high-k oxides. Such insights provide practical guidelines for enabling selective integration of HfO_2 and ZrO_2 in next-generation transistors and interconnect architectures, where atomic-scale precision and material specificity are indispensable.

9:15am **AP+EM+PS+TF-FrM-5 Area Selective ALD for Future Engineering Challenges**, ***Stacey Bent***, Stanford University **INVITED**

The continued downscaling of electronic device dimensions requires the development of new, precise patterning methods that are compatible with high-volume manufacturing. Atomic level processing, and in particular area selective atomic layer deposition (AS-ALD), continues to gain attention as an important method to achieve nanoscale features at the sub-10 nm length scale. It is well known that tuning the surface chemistry of the substrate can be used to either inhibit or enhance ALD nucleation, leading to selective deposition. A key strategy for AS-ALD has been the use of

inhibitors which can alter the native surface reactivity to block nucleation in thermal as well as plasma-assisted ALD. This inhibition approach enables good selectivity in AS-ALD of thin films on a variety of substrate materials, including dielectrics and metals, and I will present several inhibitor-based AS-ALD systems. Importantly, the ALD precursor also plays a key role in influencing selectivity. Results show that precursor size can have a significant influence on the ability of inhibitors to prevent ALD nucleation. However, precursor size alone is not the defining metric, and I will share examples that highlight the influence of other precursor effects, such as precursor-inhibitor reactivity and miscibility. Ultimately, developing molecular design rules for both inhibitors and ALD precursors will be critical for applying AS-ALD more widely to future challenges in microelectronics fabrication.

9:45am **AP+EM+PS+TF-FrM-7 Controlling ASD of a Multi-Color System: PEDOT ASD between SiN, Si-H, and SiO2 by Pre-Treatment Adjustment**, ***Jeremy Thelven***, *Nicholas Carroll, Gregory Parsons,* North Carolina State University

Complex 3D device architectures are proposed as the solution to make devices more energy efficient.[1] These architectures require many lithographic steps where the high costs of EUV lithography limits device throughput. As such, there is a need for process augmentation to reduce the EUV burdening. A potential solution is area-selective deposition(ASD), where film deposition occurs on a "growth" surface while it is inhibited on an adjacent "non-growth" surface allowing for bottom-up processing.

While ASD conveys the notion of selective deposition between two surfaces, however, in fabrication more might be exposed. Therefore, it is crucial to look at multiple surfaces, a "multi-color system." The goal being to have the versatility of depositing the desired material only on the desired location(s). It is then important to know processes that activate or deactivate specific surfaces in a multi-color system.

Poly(3,4-ethylenedioxythiophene)(PEDOT) was deposited by oxidative chemical vapor deposition(oCVD) using 3,4-ethylenedioxythiophene(EDOT) monomer and antimony pentachloride($SbCl_5$) as reactants to analyze how various pre-treatment strategies can tune the ASD between Si-H, SiN, and SiO_2 surfaces. As a control, single-material coupons were treated with a diluted hydrofluoric acid(DHF) wet etch prior to PEDOT oCVD. Results showed ~30nm of ASD on SiN and SiO_2 vs. Si-H. Three different pre-treatment strategies were evaluated: 1 cycle of molybdenum hexafluoride(MoF_6)/N_2, 7 cycles of N,Ndimethylamino-trimethylsilane(DMATMS)/N_2, and 7 cycles of DMATMS/N_2 followed by a water soak. Ellipsometer, water contact angle, XPS, and SEM results show that MoF_6 served to simultaneously activate and deactivate the Si-H and SiO_2, respectively, allowing for PEDOT ASD on SiN and Si-H vs. SiO_2. DMATMS exposure deactivated only the SiO_2 showing PEDOT ASD on SiN vs. SiO_2 and Si-H. Including a water soak after the DMATMS activated the Si-H to PEDOT deposition resulting in a deposition configuration of Si-H and SiN vs. SiO_2.

Overall, the concept of tunable selectivity for a three-color system is demonstrated by these results. These pre-treatment strategies providing a better understanding into controlling selectivity.

1.Datta, S.; Chakraborty, W.; Radosavljevic, M. Toward. *Science* **2022**, *378* (6621), 733–740.

10:00am **AP+EM+PS+TF-FrM-8 Kinetics Model for Selective Thermal Etching of $Si_{1-x}Ge_x$ in F_2/Ar**, ***Yi Chen***, *Daniel Cho,* University of California, Los Angeles*; John Hoang, Nicholas Altieri, Ji Zhu, Samantha Tan,* Lam Research Corporation*; Jane Chang,* University of California, Los Angeles

The selective etching of $Si_{1-x}Ge_x$ over Si enables the fabrication of the gate-all-around field-effect transistors. Thermal etching of Si/$Si_{1-x}Ge_x$ at near room temperature features high selectivity, exhibiting a non-linear relationship between etch rate and Ge% (Fig. 1(a)). There are no reported reaction mechanisms explaining this unique Ge%-dependent phenomenon.

In this work, thin films of $Si_{1-x}Ge_x$ of varying Ge content (Ge% = 0 to 1) were etched thermally by molecular F_2 gas at near room temperature under different F_2 partial pressures (0.5 to 10 mTorr) in Ar. The etch rates were quantified by ellipsometry measurement and the relationship between etch rate and Ge% resembled those shown in Fig. 1(a). Reported $Si_{1-x}Ge_x$ etch selectivity ranges from 100 to 1000 and the unpublished maximum etch selectivity is from 200 to 250. The unpublished experimental data is being reviewed for public release and will be presented at the conference. A kinetics model was established in this work to elucidate the reaction pathways in thermal etching of $Si_{1-x}Ge_x$ by F_2, considering reactions between atomic fluorine and various surface species and the interplay between reaction products involving Si and Ge. The model result (Fig. 1(b)) yielded the unique volcano-shaped relationship between etch rate and Ge%, validating the reactions considered in the model captured the main kinetics during F_2 etching of $Si_{1-x}Ge_x$.

10:30am **AP+EM+PS+TF-FrM-10 Area-Selective Deposition by Surface Engineering for Applications in Nanoelectronics: Enablement of 2d and 3d Device Scaling and Self-Alignment**, ***Silvia Armini,*** IMEC Belgium **INVITED**

At advanced nodes targeting 10 nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error,...). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore's law. On the other hand, 2D scaling is reaching its limitations driving the transition to 3D and vertical integration schemes (such as 3DNAND, 3DDRAM, CFET...), which result in higher devices density per unit area and lower production cost. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. In addition, ASD allows coping with high aspect ratio and complex 3D architectures. The strong sensitivity of ALD to surface chemistry and its self-limiting nature are particularly appealing for ASD.

In this talk I will illustrate a variety of ASD processes and applications spanning from nano-interconnects, logic and memories to patterning.

11:00am **AP+EM+PS+TF-FrM-12 MO-Mo? Oh No! The Problem of Carbon in Metalorganic Molybdenum Deposition**, ***Kyle Blakeney***, *David Mandia, Matthew Griffiths, Jeong-Seok Na, Raihan Tarafdar, Jeremie Dalton,* Lam Research Corporation

Molybdenum (Mo) halides and oxyhalides comprise the sole class of precursors that can deposit Mo metal films by ALD/CVD with sufficient purity for applications in advanced microelectronic devices. Unfortunately, solid, low vapor pressure Mo chloride precursors have challenges in flux stability and low vapor pressure. Metalorganic (MO) precursors are commonly used to address some of these challenges and are useful alternatives to halides for many non-metal films such as SiO_2, SiN, TiN, Al_2O_3, etc. Despite much effort, MO-precursors have not met the performance of chloride precursors for depositing pure Mo.

This presentation will summarize key findings of MO-Mo process development by the Lam ALD/CVD Metals concept and feasibility (C&F) group. Included will be typical precursor tests using coupon process modules, 300mm C&F chambers, fundamental mechanistic investigations of Mo surface reactivity, and novel deposition pathways such as conversion-reduction (Figure 1) and alloy formation (Figure 2).

11:15am **AP+EM+PS+TF-FrM-13 The Effects of Process Chemistry on Blocking Chemisorption in ALD: Thin Film Precursor, Co-Reactant and Co-Adsorbate**, *Jay Swarup, James Jensen, Jeffrey Gao,* ***James Engstrom***, Cornell University

Achieving area selective deposition requires preventing growth on the non-growth surface (NGS), which often involves the use of molecules to block growth on those surfaces. Careful choice of the ALD process chemistry, thin film precursor and co-reactant, as well as the blocking molecule and how it is administered, is important. We report here a systematic examination of the effects of the precursor, co-reactant and co-adsorbate/blocking molecule on preventing growth of Al_2O_3 on SiO_2. We also consider the effects of temperature, and the dosing sequence employed for the blocking species. Concerning the precursor we compare trimethylaluminum (TMA) to a non-pyrophoric precursor containing only Al-N bonds and no Al-C bonds, *i.e.*, BDMADA-Al **[1]**. For co-reactants we compare H_2O to *t*-BuOH. Finally, we consider two blocking species: octadecyl trichlorosilane (ODTS), and dimethylamine trimethylsilane (DMATMS). In this study we employ a quartz-crystal microbalance to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized *ex situ* using X-ray photoelectron spectroscopy, and a variety of techniques. Concerning the "pristine" processes, *i.e.*, ALD in the absence of a blocking molecule, the properties of the films (density, C incorporation, stoichiometry, growth rates) are comparable using either BDMADA-Al or TMA as the precursor under similar reaction conditions. These species also react similarly with H_2O and *t*-BuOH as the co-reactant, where steady growth with the latter is only observed at sufficiently high temperatures. Concerning blocking growth, we have observed a number of identifiable trends. First, employing the same ALD process chemistry, ODTS produces better blocking in comparison to DMATMS in cases involving a single dose of the blocking molecule. When comparing TMA and BDMADA-Al, we observe that for

both blocking molecules that the latter is more efficiently blocked. These two observations demonstrate the importance of molecular size as the larger BDMADA-Al is more efficiently blocked, and the larger ODTS is better for preventing growth. Temperature has a definitive effect on the efficiency of preventing growth where we find that higher temperatures lead to more effective blocking of growth. The dosing sequence employed for the blocking species also plays an important role. Repetitive dosing of DMATMS in an “ABC” process provides superior blocking with respect to a single pre-exposure, and these results exceed those produced by ODTS.

[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).

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