

## Atomic Scale Processing Focus Topic

### Room On Demand - Session AP-Contributed On Demand

#### Atomic Scale Processing Contributed On Demand Session

**AP-Contributed On Demand-1 Cu<sub>2</sub>O Spontaneous Etching By Acetylacetone and Cu Atomic Layer Etching Using Sequential O<sub>2</sub> or O<sub>3</sub> and Acetylacetone Exposures,** *Aziz Abdulagatov, J. Partridge*, University of Colorado at Boulder; *V. Sharma, C. Dezelah*, ASM Microchemistry Ltd., Finland; *S. George*, University of Colorado at Boulder

Copper atomic layer etching (ALE) has been performed earlier using sequential exposures of O<sub>2</sub> or O<sub>3</sub> and hexafluoroacetylacetone (Hhfac) [1]. To avoid halogens in the reactants, this study explored Cu ALE using O<sub>2</sub> or O<sub>3</sub> and acetylacetone (Hacac) (See Supplemental Figure 1). Cu<sub>2</sub>O spontaneous etching and Cu ALE were measured using in situ spectroscopic ellipsometry (iSE). The oxidation of the copper films was also examined including the effect of the O<sub>2</sub> or O<sub>3</sub> exposures on the surface morphology, chemical state and crystallographic structure. Additional studies were performed on Cu<sub>2</sub>O powders to identify volatile etch products and structural changes after Hacac exposures.

The copper oxide films were obtained by O<sub>2</sub> or O<sub>3</sub> oxidation of metallic copper films at 250°C. Atomic force microscopy (AFM) measurements revealed that Cu oxidation produced rough surfaces. X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measurements showed that the oxidized films were crystalline cubic Cu<sub>2</sub>O. The iSE measurements determined that the thickness of these Cu<sub>2</sub>O films was reduced linearly by consecutive exposures of Hacac during spontaneous etching. Additional iSE analysis determined that Cu ALE using sequential exposures of O<sub>2</sub> and Hacac removed Cu at 4.1 Å/cycle at 250°C (See Supplemental Figure 2). This etch rate during Cu ALE was obtained using reactant pressures of 20 and 0.250 Torr, and dose times of 0.5 and 1 s, for O<sub>2</sub> and Hacac, respectively.

Quadrupole mass spectrometry (QMS) investigations were conducted using Hacac exposures on Cu<sub>2</sub>O powders at 250°C to identify the volatile etch products. H<sub>2</sub>O was observed as a product at the beginning of the Hacac exposure. H<sub>2</sub>O is consistent with the disproportionation reaction Cu<sub>2</sub>O + 2Hacac → Cu(acac)<sub>2</sub> + Cu + H<sub>2</sub>O. To verify the production of Cu during this disproportionation reaction, XRD analysis was performed on the Cu<sub>2</sub>O powders after the Hacac exposures. The XRD results confirmed that Cu<sub>2</sub>O was partially converted to Cu by the Hacac exposures. QMS also searched for the Cu(acac)<sub>2</sub> reaction product from the disproportionation reaction. Although no Cu(acac)<sub>2</sub> was detected by QMS, Fe(acac)<sub>2</sub> was observed from the exchange of Cu(acac)<sub>2</sub> with Fe on the reactor walls.

[1] E. Mohimi, X.I. Chu, B.B. Trinh, S. Babar, G.S. Girolami and J.R. Abelson, *ECS J. Solid State Sci. Technol.* **7**, P491 (2018).

**AP-Contributed On Demand-4 In-situ Analysis of Surface Reactions for Plasma-Assisted Thermal-Cyclic Atomic Layer Etching of Tantalum Nitride,** *Kazunori Shinoda*, Hitachi, Japan; *M. Hasegawa*, Nagoya University, Japan; *H. Hamamura*, Hitachi, Japan; *K. Maeda, K. Yokogawa, M. Izawa*, Hitachi High-Tech, Japan; *K. Ishikawa, M. Hori*, Nagoya University, Japan

Isotropic atomic layer etching (ALE) offers the potential of atomically precise material removal with high conformality and high selectivity for future three-dimensional devices including nano-sheet gate-all-around field effect transistors (FETs). The authors have developed isotropic ALE for various materials such as Si<sub>3</sub>N<sub>4</sub> and TiN by using the surface reactions of ammonium salt-based modified layers in CHF<sub>3</sub>/O<sub>2</sub> plasma [1, 2]. Although this kind of plasma is suited for forming ammonium salt-based modified layers on Si<sub>3</sub>N<sub>4</sub> and TiN films, erosion of carbon hard masks is a concern due to the use of oxygen. In this work, both conventional CHF<sub>3</sub>/O<sub>2</sub> plasma and an oxygen-free fluorocarbon-based plasma have been compared by using in-situ X-ray photoelectron spectroscopy (XPS) to examine the surface reactions for plasma-assisted thermal-cyclic ALE of TaN.

Cycles involving CHF<sub>3</sub>/O<sub>2</sub> plasma exposure and heating were repeated. The exposure to CHF<sub>3</sub>/O<sub>2</sub> plasma produced a modified layer on TaN. In-situ XPS analysis revealed that the TaN surface was modified in the plasma by forming N-H bonds and Ta-O-F bonds. The layer thickness was self-limiting with respect to the plasma-exposure time. After heating, non-volatile tantalum oxides remained on the TaN surface due to oxidation of the surface.

Cycles involving oxygen-free fluorocarbon-based plasma exposure and heating were repeated for developing TaN ALE to suppress oxide residues. This plasma consisted of hydrogen and fluorine that could form an

ammonium-salt-based modified layer in both Si<sub>3</sub>N<sub>4</sub> and TiN ALE, and it did not consist of oxygen that could erode carbon hard masks. The modified layer was produced on TaN after exposure to the plasma at -20°C. In-situ XPS analysis revealed that the layer contained N-H bonds and Ta-F bonds. The modification of the TaN surface in the plasma was self-limiting with respect to the plasma-exposure time. After heating, both the N-H bonds and Ta-F bonds disappeared completely. This result suggests that the modified layer was removed by heating. Thus, an applicable process for using carbon hard masks has been successfully demonstrated, and its surface reactions for thermal-cyclic ALE of TaN have been analyzed.

[1] K. Shinoda, N. Miyoshi, H. Kobayashi, M. Izawa, K. Ishikawa, and M. Hori, *J. Phys. D: Appl. Phys.* **52**, 475106 (2019).

[2] K. Shinoda, N. Miyoshi, H. Kobayashi, M. Izawa, T. Saeki, K. Ishikawa, and M. Hori, *J. Vac. Sci. Technol. A* **37**, 051002 (2019).

**AP-Contributed On Demand-7 A first-principle Investigation of the ALD Selectivity Driving Forces for the Area Deposition of TiO<sub>2</sub>,** *Yukio Kaneda*, Sony Semiconductor Solutions Corporation, Japan; *E. A. Marques*, Katholieke Universiteit Leuven, Belgium; *S. Armini, A. Delabie, M. van Setten, G. Pourtois*, IMEC, Belgium

Area selective deposition (ASD) is one of the advanced patterning technologies for further nano-scale devices. ASD enables the growth of a film on certain substrates (referred to as growth areas in what follows) and not on the other (labeled as non-growth). However, it is commonly observed that the process is poisoned by an uncontrolled deposition in an undesired area, typically protected by a surface inhibiting treatment, hence leading to a selectivity degradation. The latter is explained by the absorption of precursors in a non-growth area that acts as a seed for the nucleation of particles. [1] Though diffusion aspects are playing a key role in the process, a large part of the selectivity is also controlled by the reactivity (thermodynamic) driving forces between the precursors and the substrates. Next to the selection of the ALD precursor, it is also crucial to understand how much other molecules and by-products, such as the compounds generated by the desorption of surface inhibitors, or by the decomposition of the ALD precursors, impact on the selectivity.

Therefore, improving an ASD process requires gaining a fundamental understanding on the different mechanisms that drive the selectivity degradation. In this context, we studied the thermodynamic driving force of different key chemical reactions occurring during the ALD deposition of TiO<sub>2</sub>, including precursor adsorption on the surfaces of the growth and non-growth area, precursor decomposition and clustering, reactions with by-products and inhibitor desorption, and analyzed the mechanism of selectivity degradation by first-principle calculations with statistical thermodynamic considerations.

In this presentation, we will illustrate how the combination of atomistic simulations with thermodynamic considerations helps to understand the precursor dependency reported for the selective deposition of TiO<sub>2</sub> on SiO<sub>2</sub> and on silylated surfaces by Soethoudt *et al.* [2] We hence modeled silicon/silicon oxide surface models terminated by either hydroxyl groups (to mimic a growth area) or tri-methyl-silyl groups (ALD inhibitor), and TiCl<sub>4</sub> and H<sub>2</sub>O as the precursor and the oxidizer, respectively. From this analysis, we reproduced the temperature dependence of the selectivity. We also attributed the mechanism of selectivity degradation to the desorption of the methyl-silyl groups which is driven by temperature and reaction by-products.

We then expanded the exercise to a set of 25 commercially available Ti precursors and ranked their performances in terms of selectivity.

[1] Fabio Grillo, *et al.*, *Chemistry of Materials* **202032** (22), 9560-9572

[2] Job Soethoudt, *et al.*, *The Journal of Physical Chemistry C* **2020124** (13), 7163-7173

**AP-Contributed On Demand-10 Scaling of InGaZnO to sub-40nm Regime Using Advanced Etch Techniques,** *Shreya Kundu, F. Lazzarino*, IMEC, Belgium

Since early 2000s, InGaZnO (IGZO)-based semiconductor oxide has been studied and prototyped as advanced thin film transistors (TFTs) in transparent electronic devices like high-definition flat panel displays<sup>1</sup>. Owing to a range of attractive properties such as high carrier mobility (w.r.t amorphous silicon), low OFF state leakage, and optimal BEOL compatibility; IGZO-TFTs are now being presented as the next-generation candidate for the DRAM technology<sup>2</sup>. In addition, due to its possibility to offer high current density, it is also being considered as Schottky diode-based selectors for high density cross-point memory applications<sup>3</sup>. While these attributes make IGZO a compelling novel material to investigate, a key

challenge to enable its successful integration is its patterning into features of desired dimensions, especially at high scaling densities. Generally, metallic alloys are etched using halogen plasmas. However, a layer of IGZO exposed to a halogen produces non-volatile halide residues thereby creating a chemical etch stop and an incomplete patterning process. It has been reported that hydrocarbons (i.e. CH<sub>4</sub>) can be used to pattern large IGZO structures as the organometallic by-products formed from IGZO are volatile<sup>4</sup>. Nevertheless, there is a trade-off – hydrocarbons are mainly used as passivating agents during conventional etching. This passivating effect from hydrocarbons is magnified at tighter pitches creating a chemical etch stop yet again. In short, the scalability of IGZO features using hydrocarbon etch pose a significant challenge. In this work, we evaluate the dual role of CH<sub>4</sub> during the patterning of IGZO for a range of CD/pitch combinations. Advanced etching methods i.e. CH<sub>4</sub>-based atomic layer etching and plasma pulsing are used to enable high-density IGZO patterning<sup>5,6</sup>. We are successfully able to demonstrate well-separated IGZO features of CDs ≤ 20 nm in pitches down to sub-40 nm regime. This newly tailored etch is observed to be robust across different feature sizes and spacings, clearly exhibiting its potential to become a universal etch approach for IGZO as well as for IGZO-like materials such as InSnO and InZnO. The patterning effort focused on ensuring smooth sidewalls with negligible redeposition; limited tapering; good selectivity to electrode contact-friendly hard masks; minimal damage to IGZO stoichiometry and crystallography; and most importantly, emphasized the repeatability and uniformity generated from this advanced etch scheme.

**REFERENCES:** 1. Nature 432, 488–492 (2004); 2. IEEE Journal of the Electron Devices Society, 7, 495-502 (2019); 3. IEEE Electron Device Letters, 2014, 35, 642-644 (2014); 4. Plasma Science and Technology, 14, 10 (2012); 5. J. Vac. Sci. Technol. A 33, 020802 (2015); 6. J. Vac. Sci. Technol. A 30, 040801 (2012)

**AP-Contributed On Demand-13 A Theoretical Investigation Into the Oxidative Etching of Ruthenium, Neung-Kyung Yu, B. Shong**, Hongik University, Korea (Republic of); J. Lee, W. Kim, Hanyang University, Korea (Republic of)

**A theoretical investigation into the oxidative etching of ruthenium**

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Ruthenium (Ru) is a transition metal with low resistivity especially on a nanometer scale, making it a promising candidate for future interconnect applications. Ru can be oxidized and dry etched through the formation of volatile RuO<sub>4</sub> under oxidizing conditions [1]. This distinctive property makes Ru easily compatible with atomic layer etching (ALE) process, if a self-limiting process condition for the etch rate can be found. Moreover, since atomic layer deposition (ALD) of Ru utilizes oxidative counter-reactants, Ru can be used in bottom-up selective patterning processes combining ALD and selective etching [2]. Meanwhile, the atomistic mechanism of the oxidative etching process of Ru is not yet thoroughly determined. In this work, the mechanism of surface oxidation and dry etching of Ru under ozone environment is investigated using density functional theory (DFT) calculations. The explored pathways include surface oxidation of Ru and formation of ruthenium oxide (RuO<sub>2</sub>), from both of which desorption of RuO<sub>4</sub> is considered. Our results suggest that direct etching from oxidized Ru surface is preferable to the decomposition of RuO<sub>2</sub> surface, indicating that there might be a process window for quasi-ALE of Ru.

**References** [1] Nakahara, M. et al. Etching technique for ruthenium with a high etch rate and high selectivity using ozone gas. J. Vac. Sci. Technol. B 19, 2133 (2001). [2] Vos, M. et al. Area-Selective Deposition of Ruthenium by Combining Atomic Layer Deposition and Selective Etching. Chem. Mater. 31 (11), 3878 (2019).

**AP-Contributed On Demand-16 Blocking Thermal Atomic Layer Etching With Removable Etch Stop Layers, David Zywotko**, University of Colorado Boulder; O. Zandi, J. Faguet, P. Abel, TEL Technology Center, America, LLC; S. George, University of Colorado Boulder

Thermal atomic layer etching (ALE) can be performed using sequential fluorination and ligand-exchange reactions. For example, thermal Al<sub>2</sub>O<sub>3</sub> ALE can be achieved using HF for fluorination and Al(CH<sub>3</sub>)<sub>3</sub> (trimethylaluminum (TMA)) as the metal precursor for ligand-exchange [1]. Sequential exposures of HF and TMA lead to Al<sub>2</sub>O<sub>3</sub> etch rates of 0.47 Å/cycle at 285°C.

The ability to block thermal ALE selectively will be useful for advanced nanofabrication. This study demonstrates how thermal Al<sub>2</sub>O<sub>3</sub> ALE can be blocked with removable ZrF<sub>4</sub> etch stop layers. In situ quartz crystal microbalance (QCM) measurements were utilized to monitor the etching and the effect of the etch stop layers.

The ZrF<sub>4</sub> etch stop layers could be deposited on Al<sub>2</sub>O<sub>3</sub> using tetrakis(ethylmethylamido) zirconium and H<sub>2</sub>O at 285°C. These reactants deposit ZrO<sub>2</sub> layers that are then converted to ZrF<sub>4</sub> during the subsequent HF exposure. Because Al(CH<sub>3</sub>)<sub>3</sub> does not undergo ligand-exchange with ZrF<sub>4</sub> [2], the ZrF<sub>4</sub> layer serves as an etch stop layer. QCM measurements revealed that an initial ZrO<sub>2</sub> thickness of just one monolayer prior to fluorination was able to stop completely the thermal Al<sub>2</sub>O<sub>3</sub> ALE. Prior to reaching a ZrO<sub>2</sub> thickness of one monolayer, the etching inhibition was proportional to the ZrO<sub>2</sub> fractional coverage. The ZrF<sub>4</sub> etch stop layer was observed to arrest the thermal Al<sub>2</sub>O<sub>3</sub> ALE for >100 ALE cycles.

The ZrF<sub>4</sub> etch stop layer could then be easily removed by a ligand-exchange reaction with AlCl(CH<sub>3</sub>)<sub>2</sub> (dimethylaluminum chloride (DMAC)) [3]. The ZrF<sub>4</sub> etch stop layer could be applied and removed repeatedly without changing the Al<sub>2</sub>O<sub>3</sub> etch rate. X-ray photoelectron spectroscopy (XPS) studies confirmed the removal of Zr on the Al<sub>2</sub>O<sub>3</sub> surface after 7 cycles of DMAC and HF sequential exposures. Area selective deposition of the ZrF<sub>4</sub> etch stop would lead to area selective etching using HF and TMA as the reactants. Area selective deposition could be achieved based on selective reactant adsorption or substrate-dependent nucleation delays.

[1] Younghee Lee, Jaime W. DuMont and Steven M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al<sub>2</sub>O<sub>3</sub> Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

[2] Younghee Lee, Craig Huffman and Steven M. George, "Selectivity in Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions", *Chem. Mater.* **28**, 7657 (2016).

[3] Younghee Lee and Steven M. George, "Thermal Atomic Layer Etching of Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and ZrO<sub>2</sub> Using Sequential Hydrogen Fluoride and Dimethylaluminum Chloride Exposures", *J. Phys. Chem. C* **123**, 18455 (2019).

**AP-Contributed On Demand-19 Atomic Layer Etching of HfO<sub>2</sub> and ZrO<sub>2</sub> Landing on WS<sub>2</sub> Transition Metal Dichalcogenide, Jean-Francois de Marneffe, D. Marinov**, imec v.z.w., Belgium; A. Goodyear, Oxford Instruments Plasma Technology, UK; B. Groven, imec v.z.w., Belgium; P. Wyndaele, KU Leuven, Belgium; S. Kundu, imec v.z.w., Belgium; M. Cooke, Oxford Instruments Plasma Technology, UK; S. De Gendt, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (2D-TMDCs) are considered as alternative channel materials for next generation CMOS logic technology. Very large scale integration (VLSI) manufacturing requires to comply as much as possible to established processing methods and device geometries. For building VLSI compliant 2D transistor devices, the current strategy for channel gating relies on the growth of high-k oxide dielectrics (with EOT < 1nm). Electrical contacts are built by a subtractive approach where the passivating dielectric is etched away, exposing the 2D channel, then filled with the relevant metal. The present work describes the plasma etching of thin high-k dielectric stopping on WS<sub>2</sub>, aiming at contacts fabrication. Three-layer WS<sub>2</sub> films were grown on SiO<sub>2</sub> by PEALD. After WS<sub>2</sub> growth, a Si nucleation layer (0.4, 0.7 or 1.0 nm, all non-continuous) was deposited using molecular beam deposition, which was oxidized by ambient exposure prior to high-k deposition. Afterwards, HfO<sub>2</sub> and ZrO<sub>2</sub> high-k dielectrics were deposited by ALD, targeting a thickness of 6 nm. Etch screening studies and process optimization were performed on HfO<sub>2</sub>, ZrO<sub>2</sub> and PECVD SiO<sub>2</sub> films deposited directly on Si (without WS<sub>2</sub>). The high-k films were etched in a ICP chamber, modified to enable atomic layer etching (ALE). The ALE plasma conditions used in this work were based on a continuous Ar discharge which was maintained all along the ALE cycles. The cycles were consisting of two main steps of a few seconds each, separated by purges: a short pulse (without bias) during which reactive gases were injected in the plasma (BCl<sub>3</sub> or Cl<sub>2</sub>/BCl<sub>3</sub>), followed by a biased step with only Ar. The first part of the study investigates the etch of ZrO<sub>2</sub> and HfO<sub>2</sub> using pure BCl<sub>3</sub> and Cl<sub>2</sub>/BCl<sub>3</sub> plasmas. With pure Ar bombardment, the etch rate is zero until the bias power reaches ~ 15W. The addition of chlorine-based reactants enables etch at lower bias. Pure BCl<sub>3</sub> shows a non-negligible chemical etch component in the removal process. For the Cl<sub>2</sub>/BCl<sub>3</sub> mixture, the etching requires a minimal bias of 5 W to proceed, indicating that the removal process is sputter enabled. The ALE synergy (at 8W bias) is calculated, giving S~53% for the pure BCl<sub>3</sub> discharge, while S=100% for the

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Cl<sub>2</sub>/BCl<sub>3</sub> mixture (for both ZrO<sub>2</sub> and HfO<sub>2</sub>). Applying the optimal ALE etch processes to a WS<sub>2</sub> films passivated with ZrO<sub>2</sub> or HfO<sub>2</sub>, it is found that the high-k layers are fully removed, without major change in the composition of the underlying WS<sub>2</sub>. The low damage high-k removal is confirmed by Raman spectroscopy, which show negligible changes after complete high-k etch.

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**AP-Contributed On Demand-22 Probing the Selectivity of Area-Selective Spatial ALD + Etch-Back Supercycles for SiO<sub>2</sub> by Low Energy Ion Scattering, Alfredo Mameli**, TNO-Holst Centre, Netherlands; *P. Brüner*, IONTOF GmbH, Germany; *F. Roozeboom*, TNO-Holst Centre, Netherlands; *T. Grehl*, IONTOF GmbH, Germany; *P. Poodt*, TNO-Holst Centre, Netherlands

Area-selective ALD interleaved with etch-back steps in a supercycle fashion has recently been reported as very effective in achieving high selectivity. Such supercycles can result in lower defectivity on the non-growth area and thicker layers on the growth area, as compared to solely area-selective ALD.<sup>1,2</sup> The complementarity of deposition and etching techniques can therefore offer great potential for reaching the ultimate requirements in advanced device manufacturing.

Here we use low energy ion scattering (LEIS) to probe the selectivity of the first supercycle, consisting of plasma-enhanced selective spatial-ALD of SiO<sub>2</sub> and conventional CF<sub>4</sub>-based reactive ion etching (RIE). Given its extreme sensitivity to the top monolayer(s) of a thin film, LEIS can reliably quantify the selectivity and defectivity on the non-growth areas in terms of surface coverage and derived thickness.

For the selective spatial ALD a three-step approach was adopted,<sup>3</sup> consisting of successive inhibitor, silicon precursor (BDEAS) and O<sub>2</sub> plasma exposures. Silicon wafers (growth area) with large ZnO patterns (non-growth area) were used as substrates. After 20 spatial ALD cycles, no silicon was detected on the non-growth area by LEIS (detection limit 2 % SiO<sub>2</sub> surface coverage), implying excellent process selectivity. The selectivity is however gradually lost by increasing the number of ALD cycles up to 110. On the non-growth area, the SiO<sub>2</sub> layers now had an averaged thickness of 3.5 nm as measured by spectroscopic ellipsometry (SE) and corroborated by LEIS measurements (86% Si surface coverage). At the same time on the growth area, a SiO<sub>2</sub> thickness of 11 nm was measured. In order to correct for the selectivity loss, a 3 seconds RIE step was applied, which restored the Si coverage and reduced the SiO<sub>2</sub> thickness on top of the non-growth area back to zero, as demonstrated by LEIS. Concurrently, 8 nm thick SiO<sub>2</sub> was left on the growth area.

The data presented in this work demonstrate the effectiveness of combining selective spatial ALD + etch-back corrections to achieve extreme SiO<sub>2</sub> selectivity while retaining high deposition rates. Furthermore, we will discuss how LEIS can provide useful information on selectivity as well as defect formation on the non-growth area. Finally, we have extended the plasma-enhanced selective spatial ALD of SiO<sub>2</sub> to other non-growth areas.

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[3] A. Mameli *et al.*, *ACS Nano*, **11**, 9303-9311 (2017).

**AP-Contributed On Demand-25 CMOS-Compatible Processing of Atomic-Precision Donor Devices, DeAnna Campbell**, A. Leenheer, E. Anderson, S. Schmucker, J. Ivie, X. Gao, W. Lepkowski, T. Lu, L. Tracy, S. Misra, Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) is a technique for placing dopant atoms with single atomic-lattice site precision on silicon surfaces. For example, phosphorous adsorbed on a clean Si surface then capped with Si can form a monolayer (delta layer) of donors with optional selected-area patterning. The dopant atoms are incorporated into the silicon lattice through a surface-activated chemical reaction rather than a thermally activated diffusion process, **allowing for electrically active doping above the solubility limit for phosphorus in silicon**. The two-order of magnitude higher doping levels and two-dimensional nature of the dopant sheet enable new device physics and the potential for new device types and geometries.

Atomic precision fabrication requires atomically clean surfaces. Historically the APAM technique has used surface preparation techniques with high temperatures in excess of 1200 °C, but recent modifications of the surface preparation process have lowered this temperature to 800-900 °C, opening integration possibilities with CMOS. In this talk we report on the initial

development of a CMOS process flow incorporating APAM doping. Based on the thermal budget and processing constraints, our basic process flow involves building the APAM device between CMOS Front-end-of-line (FEOL) and the CMOS Back-end-of-line (BEOL) steps. We will discuss possible insertion points for the APAM processing in a CMOS flow, considering possible effects on (existing) transistor channels, gate oxides, and contacts. Two additional mask layers are added, termed "APAM select" to indicate a window for APAM device processing and "APAM active" to define the actual APAM device area. We will report progress on development devices including die-level and wafer-level testing of discrete transistors and simple integrated circuits that incorporate APAM processing and wiring. We conclude with a discussion of future integration challenges such as wafer scale processing of APAM devices in a CMOS foundry flow. Direct integration of APAM components into CMOS circuits opens the door for devices with enhanced functionality.

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**AP-Contributed On Demand-28 Room Temperature Operation of Donor-Based Atomically Precise Devices, Jeffrey Ivie**, L. Tracy, J. Mendez, S. Gao, E. Anderson, S. Schmucker, D. Campbell, D. Scrymgeour, A. Katzenmeyer, D. Ward, T. Lu, S. Misra, Sandia National Laboratories

Atomic precision advanced manufacturing (APAM) of electrical devices, fabricated using hydrogen depassivation lithography in a scanning tunneling microscope, offer a way to explore device physics with the ultimate degree of control. Almost all previous work has focused on demonstrations of basic physics principles, using devices operating at cryogenic temperatures. However, these devices are isolated through freezing out leakage pathways and cannot function at room temperature, making them incompatible for large-scale integration with modern metal-oxide semiconductor (MOS) technologies. New device designs to suppress leakage pathways are critical for advancing MOS compatible APAM devices forward.

To enable room temperature operation of AP devices, we have developed a MOS compatible counter-doping scheme, which provides significant leakage current isolation around the APAM device. Refinements to the low thermal budget processes for sample preparation and epitaxial Si growth of capping material were critical for maintaining proper dopant profiles. Room temperature electrical measurements on APAM devices demonstrate electrical properties on par with devices measured at cryogenic temperatures. These electrical properties also compare well with carrier concentration and mobility extracted from room temperature spectroscopic ellipsometry measurements. This demonstration of a MOS compatible doping scheme enabling room temperature operation opens the door for integration of APAM devices with MOS technology.

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**AP-Contributed On Demand-31 The Interplay of Diffusion and Size-Dependent Reactivity in Ruthenium Area-Selective Deposition, Jan-Willem Clerix**, E. Marques, A. Delabie, KU Leuven / imec, Belgium

Area-selective deposition (ASD) is a promising technique for semiconductor device manufacturing. The replication of nanoscale patterns by ASD can simplify device fabrication process flows by reducing the number of lithography, etch and chemical-mechanical polishing steps. In addition, ASD could eliminate pattern overlay errors. In particular, Ru ASD is of interest for patterning applications as Ru hard masks with high etch resistance or for application in interconnect structures. (Ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O<sub>2</sub> atomic layer deposition (ALD) has been used for Ru ASD in SiO<sub>2</sub>/TiN nanopatterns [1]. However, undesired growth of Ru nanoparticles on the methyl-terminated SiO<sub>2</sub> non-growth surface limits the achievable Ru film thickness. This undesired nanoparticle growth is governed by precursor adsorption, surface diffusion of Ru adspecies and aggregation. Ru nanoparticles that are large enough (>0.85 nm) to catalyze

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O<sub>2</sub> dissociation can also grow by direct precursor adsorption on the nanoparticle.

In this study, we model how the growth mechanism influences selectivity in patterns with feature sizes of 20–200 nm. For large non-growth areas (≥100 nm wide), diffusion results in a larger amount of Ru deposited on the non-growth area than in systems without diffusion. Diffusion and aggregation result in particles, on the non-growth area, large enough (>0.85 nm) to grow by direct precursor adsorption. This direct precursor adsorption on particles is much faster than deposition on the surface. Such large particles become immobile and trapped on the non-growth surface. Conversely, for small non-growth areas (≤50 nm), diffusion of Ru adspecies from the SiO<sub>2</sub> non-growth surface to the TiN growth surface reduces defectivity in Ru ASD (Figure 1). These small diffusive Ru adspecies are effectively captured at the interfaces of the nanoscale patterns before their growth by precursor adsorption is catalyzed. For small non-growth areas (≤50 nm), diffusion to the growth area prevents the formation of particles larger than the critical diameter altogether.

Knowledge about the interplay of diffusion and size-dependent reactivity in nanoscale patterns can help in developing defect mitigation strategies. For instance, on small non-growth areas, regular isotropic etches should be successful in removing all defects while retaining a Ru film on the growth surface. This synergistic defectivity reduction should apply to all deposition processes with diffusion and size-dependent reactivity.

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**AP-Contributed On Demand-34 Thermal Atomic Layer Etching of Nickel and Cobalt Using SO<sub>2</sub>Cl<sub>2</sub> and P(CH<sub>3</sub>)<sub>3</sub>, Jessica Murdzek, S. George, University of Colorado at Boulder**

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal metal ALE is particularly challenging because the oxidation state of the metal must be changed to match the oxidation state of the volatile metal etch product. After changing the oxidation state, the metal then needs to form a stable and volatile complex. In this work, Ni and Co ALE are developed by first changing the metal oxidation state by chlorination using SO<sub>2</sub>Cl<sub>2</sub>. Subsequently, the metal is etched by the binding of P(CH<sub>3</sub>)<sub>3</sub> (PMe<sub>3</sub>) ligands that can volatilize the nickel or cobalt chloride.

The logic of this approach is based on the Covalent Bond Classification (CBC) method. The key is forming metal complexes that obey the “18 electron rule” or “16 electron rule”. X ligands are one-electron donors like Cl. L ligands are two-electron donors like PMe<sub>3</sub>. According to the CBC method, nickel complexes typically have NiX<sub>2</sub>L<sub>3</sub> or NiX<sub>2</sub>L<sub>2</sub> configurations, and cobalt complexes are typically found in the CoX<sub>2</sub>L<sub>4</sub>, CoX<sub>2</sub>L<sub>2</sub>, or CoX<sub>3</sub>L<sub>3</sub> configurations. The goal for Ni or Co ALE is then to create these volatile metal compounds using sequential SO<sub>2</sub>Cl<sub>2</sub> and PMe<sub>3</sub> surface reactions. The proposed surface chemistry for Ni or Co ALE (Figure 1) assumes SO<sub>2</sub>Cl<sub>2</sub> exposure leads to NiCl<sub>2</sub> or CoCl<sub>2</sub>. Then the NiCl<sub>2</sub> or CoCl<sub>2</sub> is volatilized by binding with PMe<sub>3</sub>.

Both nickel and cobalt ALE have been studied with in situ quartz crystal microbalance (QCM). For nickel, one dose of SO<sub>2</sub>Cl<sub>2</sub> produces a mass gain around 70 ng/cm<sup>2</sup> at 150 °C. In comparison, for cobalt, one dose of SO<sub>2</sub>Cl<sub>2</sub> produces a mass gain around 1,000 ng/cm<sup>2</sup> at 150 °C (Figure 2). The large mass gain on cobalt indicates that, at the same temperature, much more CoCl<sub>2</sub> is formed on cobalt compared with NiCl<sub>2</sub> formed on nickel. The large surface layer of CoCl<sub>2</sub> subsequently requires many PMe<sub>3</sub> doses (20–30) for full removal. In comparison, only one dose of PMe<sub>3</sub> needed to fully remove the NiCl<sub>2</sub>. According to QCM and X-Ray reflectivity (XRR) measurements, the nickel etch rate increased with increasing temperature, from 0.14 Å/cycle at 75 °C to 3.07 Å/cycle at 175 °C. Due to high levels of chlorination for cobalt, the Co etch rates are higher than the Ni etch rates at around 3–5 Å/cycle.

**AP-Contributed On Demand-37 Molecular Mechanisms of Thermal Atomic Layer Etching of Cobalt, Iron, and their Alloys, Andrew Teplyakov, University of Delaware**

With recent advances in sub-10 nm technologies and in developing complex supercycle etching procedures for transition metals, the molecular mechanisms of thermal atomic layer etching (ALE) are quickly coming to the forefront of the tools required to achieve atomic-level control needed for the next generation of devices. The initial attempts to assume the mechanisms of thermal dry etching based on simple chemical analysis, simplified computational models, and optimization of etching procedures have been successful in explaining some of the phenomena, including basic

understanding of surface smoothing during ALE; however, utilization of realistic etching conditions, presence of multiple etchants and complex etching products, and the role of defects in surface processing require in-depth mechanistic description that is only started being developed. This presentation will focus on recent approaches that our group developed combining thermal desorption, microscopy, and surface patterning with ex-situ XPS analysis and selected computational studies to describe the molecular mechanism of thermal dry etching of cobalt, iron, and CoFeB alloy combining surface chlorination and the reactions with acetylacetonates. The same strategy can be further used to firm up our understanding of the effects of surface functionalization, defect formation, and possibly applications of combinatorial chemistry in developing modern ALE methods.

**AP-Contributed On Demand-40 Towards Ultraprecise Bipolar 2D devices using Atomic Precision Advanced Manufacturing, James H.G. Owen, R. Santini, E. Fuchs, J. Randall, Zyvex Labs; J. Mendez, X. Gao, D. Mamaluy, S. Misra, Sandia National Laboratories**

Atomic Precision Advanced Manufacturing (APAM), the ability to fabricate 2D atomic-scale devices such as the ‘single-atom transistor’ [1] and dopant patch array devices [2] via the placement of *n*-type dopants such as P and As in single planes of Si(001) has recently taken a large step forward, as the possibility of similarly placing *p*-type dopants such as B and Al has been demonstrated. While the direct equivalents of phosphine and arsine are not stable for Gr. III elements, diborane has been used to create a p-n junction[3], and for applications where few or single dopants may be required, halide precursors, BCl<sub>3</sub> and AlCl<sub>3</sub> are proving promising on H and Cl masks[4].

In this work, we demonstrate the ability to form bipolar atomic-scale devices using BCl<sub>3</sub> to place B and PH<sub>3</sub> to place P using a H mask. The process involves sequential patterning, dosing and incorporation steps for each dopant. We are developing the ability to produce a new class of bipolar devices with a number of advantages, including a significantly improved gain-bandwidth product, low-noise operation and cryogenic operation. An example of a npn junction device pattern after incorporation of both B and P dopants, but before burial of the complete device, is shown in Fig. 1. To help understand the operation of these 2D bipolar devices, we leverage Sandia’s open-source, TCAD (Technology Computer Aided Design) device simulator, Charon [5], and expand its capability to first understand previously published results on diborane-based 2D p-n junctions [3]. Once established, Charon modeling will be used to design device dimensions in the proposed bipolar devices.

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(3)Škerekň, T. et al. Bipolar Device Fabrication Using a Scanning Tunnelling Microscope. *Nat. Electron.***2020**, *3*, 524–530.

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**AP-Contributed On Demand-43 Mechanism of Thermal Dry Etching of Metallic Iron Thin Films Using Chlorine and Acetylacetone (acacH), Mahsa Konh, A. Teplyakov, University of Delaware**

Thermal dry etching of metallic iron thin films using Cl<sub>2</sub> and acetylacetone (acacH) was investigated. Iron metal is commonly used in magnetic random-access memory (MRAM) technology. The etching pathway was followed by detecting expected desorbing fragments during a heating ramp via temperature-programmed desorption (TPD) technique. The chemical properties of the etched surfaces were then analyzed with ex situ X-ray photoelectron spectroscopy (XPS). The morphology of the surface was studied with microscopic techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). To desorb volatile etch products, having an oxidized or halogenated iron surfaces is vital, since clean surfaces resulted in decomposition of the diketone ligands. The pre-chlorination of the surfaces was shown to lead to the formation of transition metals-containing products at lower temperature compared to those on oxidized surfaces. However, halogenation makes the mechanism more complicated, and the etch product can contain both Fe<sup>2+</sup> and Fe<sup>3+</sup>. These products may have a combination of ligands, and their general formula can be expressed as Fe(acac)<sub>x</sub>Cl<sub>y</sub>. To corroborate the formation Fe(acac)<sub>x</sub>Cl<sub>y</sub> from chlorinated iron surfaces reacting with acacH, density

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functional theory investigation was used. They suggest that Fe<sup>3+</sup>-based fragments are more stable than those containing Fe<sup>2+</sup> and that Fe(acac)<sub>x</sub> compounds were more stable compared to Fe(acac)<sub>x</sub>Cl<sub>y</sub> fragments.

**AP-Contributed On Demand-46 Plasma Enhanced Atomic Layer Deposition of Molybdenum Carbonitride Films,** *Ian Campbell, T. Walter, A. Molina, A. Agyapong, S. Mohney*, The Pennsylvania State University

Molybdenum nitride (MoN<sub>x</sub>) is interesting for use in thermally stable Schottky diodes. A plasma enhanced atomic layer deposition (PEALD) process was used to prepare single-phase MoN<sub>x</sub> films with some carbon incorporated with resistivity as low as 3 × 10<sup>-4</sup> Ohm-cm for 33 nm thick films. The films were prepared by plasma enhanced atomic layer deposition using bis (tert-butylimino) bis (dimethylamino) molybdenum and N<sub>2</sub>/H<sub>2</sub> in Ar for the plasma dose. The effects of plasma power and post-deposition annealing on electrical resistance and film composition were investigated. Increasing plasma power resulted in films with lower sheet resistance and higher N/Mo ratio. Annealing films caused a decrease in sheet resistance and N/Mo ratio. Carbon was present in the film, although in lower concentration than Mo and N, without much change for different plasma powers. This work was funded by the Office of Naval Research under Grant N000141812360.

**AP-Contributed On Demand-49 Thermal Atomic Layer Etching of Al<sub>2</sub>O<sub>3</sub> and AlN Using HF or XeF<sub>2</sub> for Fluorination and BCl<sub>3</sub> for Ligand-Exchange,** *Austin Cano, S. George*, University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al<sub>2</sub>O<sub>3</sub> and AlN can be performed using HF or XeF<sub>2</sub> as the fluorination reactant and BCl<sub>3</sub> as the ligand-exchange reactant. To investigate the etching mechanism, in-situ FTIR spectroscopy was used to identify the surface species and in-situ spectroscopic ellipsometry was employed to measure the etch rates. Quadrupole mass spectrometry was also employed to identify the volatile etch products. The Al<sub>2</sub>O<sub>3</sub> studies were performed using Al<sub>2</sub>O<sub>3</sub> ALD films grown using trimethylaluminum (TMA) and water as the reactants. The AlN investigations were conducted using crystalline AlN to explore the etch rates. The FTIR experiments employed AlN films grown by ALD using tris(dimethylamido)aluminum and ammonia as the reactants.

When BCl<sub>3</sub> is used as a reactant, the ALE mechanism could occur by BCl<sub>3</sub> conversion of Al<sub>2</sub>O<sub>3</sub> to B<sub>2</sub>O<sub>3</sub> or AlN to BN. Alternatively, BCl<sub>3</sub> could undergo ligand-exchange with the fluorinated AlF<sub>3</sub> surface. For thermal Al<sub>2</sub>O<sub>3</sub> ALE, FTIR studies revealed strong evidence for a conversion reaction during the initial BCl<sub>3</sub> exposure on Al<sub>2</sub>O<sub>3</sub>. The original Al-O vibrational modes were converted to B-O vibrational modes by the initial BCl<sub>3</sub> exposures as shown in Figure 1. After the first ALE cycle using sequential HF and BCl<sub>3</sub> exposures, there was no more evidence of conversion and the Al<sub>2</sub>O<sub>3</sub> etching proceeded through a fluorination and ligand-exchange mechanism. Quadrupole mass spectrometry measurements observed that BCl<sub>3</sub> exposures to AlF<sub>3</sub> yielded BCl<sub>2</sub>F and AlCl<sub>3</sub> reaction products. In situ ellipsometry measurements determined that the Al<sub>2</sub>O<sub>3</sub> ALE etch rate using HF and BCl<sub>3</sub> as the reactants varied with temperature from 0.01 Å/cycle at 270°C to 0.19 Å/cycle at 330°C.

In-situ FTIR and spectroscopic ellipsometry were also used to explore thermal AlN ALE. FTIR studies revealed that the initial BCl<sub>3</sub> exposures created a thin BN layer on the surface. Subsequent HF and BCl<sub>3</sub> exposures were consistent with AlN fluorination by HF and subsequent F/Cl exchange to form volatile AlCl<sub>3</sub> product during BCl<sub>3</sub> exposures. The Al-N vibrational stretch decreased progressively versus number of HF/BCl<sub>3</sub> cycles as displayed in Figure 2. HF was not able to fluorinate single crystalline AlN substrates. Consequently, XeF<sub>2</sub> was required as a stronger fluorination source. When combining viscous flow XeF<sub>2</sub> exposures with static BCl<sub>3</sub> exposures, ellipsometry measurements showed that AlN etching occurred at temperatures above 220°C. An etch rate of 0.81 Å/cycle was obtained at 255°C. In contrast, growth of a top layer that may be composed of AlF<sub>x</sub>Cl<sub>y</sub> was observed at lower temperatures. This top layer could be removed by long static BCl<sub>3</sub> exposures.

**AP-Contributed On Demand-55 Mechanisms of Thermal Atomic Layer Etching (ALE) of Metal by β-diketones,** *Abdulrahman H. Basher*, Center for Atomic and Molecular Technologies, Osaka University, Osaka, Japan; *I. Hamada*, Graduate School of Engineering, Osaka University, Osaka, Japan; *M. Krstić*, Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; *T. Ito, K. Karahashi*, Center for Atomic and Molecular Technologies, Osaka University, Osaka, Japan; *W. Wenzel*, Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; *S. Hamaguchi*, Center for Atomic and Molecular Technologies, Osaka University, Osaka, Japan

Thermal atomic layer etching (ALE) can be used for precise and damageless etching. For example, it can be used to fabricate magnetic tunnel junction (MTJ) stacks of magnetoresistive random-access memory (MRAM) devices [1]. The aim of this study is to understand the mechanisms of thermal ALE of metal in general, whose cycle consists of an oxidation step and an exposure step to β-diketones, such as; hexafluoroacetylacetone (hfacH), trifluoroacetylacetone (tfacH), and acetylacetone (acacH) molecules. For instance, thermal ALE of Ni with hfacH starts with the deprotonation of hfacH molecules after the oxidation of the Ni surface. By increasing the surface temperature in the range of 300 ~ 400 °C, volatile nickel complex Ni(hfac)<sub>2</sub> and water H<sub>2</sub>O molecules are formed on the surface and remove the NiO layer. In this process, once a new metallic Ni surface appears, no further etching occurs, which ensures the self-limiting nature of the thermal ALE process [2-5].

First, we examined the interaction of β-diketones with a metallic Ni surface, using a simulation code STATE [6,7]. It has been found that the cleavage of a C-F or C-H bond of a β-diketone is more likely to take place than the deprotonation on a metal surface. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. The reaction mechanisms that we observed in these simulations have revealed the self-limiting nature of thermal ALE for metals with β-diketone gases in general, which is consistent with earlier experimental observations [5,8].

Second, we examined the interaction of β-diketones with oxidized metal surfaces, using TURBOMOLE program [9]. It has been found that, as β-diketones approach an oxidized metal surface, they deprotonate. In this way, volatile metal complexes and H<sub>2</sub>O molecules can be formed when β-diketone molecules interact with an oxidized metal surface. The reaction energies of such interactions have been evaluated from the simulations and we found that oxidized metal has its own desorption energy or temperature to volatilize its metal complex. Therefore, the applied temperature can be used as a self-limiting condition if the target contains different materials. In addition, hfacH is found to get more stably bonded than acacH or tfacH with an oxidized metal surface because the negatively charged F atoms in CF<sub>3</sub> are repelled by O atoms of the surface, which forces a deprotonated hfac to adsorb on the surface nearly vertically. This does not happen to acacH, whose CH<sub>3</sub> groups tend to interact directly with the metal oxide. As a result, hfacH is considered more suited for thermal ALE processes than other β-diketones.

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**AP-Contributed On Demand-58 Orthogonal Bottom-up Nanopatterning of TiO<sub>2</sub> on SiO<sub>2</sub> and W on Si-H Using Thermal Atomic Layer Deposition and Etching,** *S. Song, Jungsik (Justin) Kim, G. Parsons*, North Carolina State University

The semiconductor industry is now entering the new era of nanopatterning in manufacturing electronic device systems, and to achieve the small node size requirement, “bottom-up” processing through area selective deposition (ASD) has been considered as a key technique. Although many individual dielectric-on-dielectric (DoD) and metal-on-metal (MoM) ASD studies have shown promising results for “bottom-up” processing, no study has demonstrated coupling of different ASD processes in a sequence. Previously, our group reported a TiO<sub>2</sub> ALD/ALE process for TiO<sub>2</sub> ASD on

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silicon dioxide (SiO<sub>2</sub>) vs hydrogen terminated silicon (Si-H). We also reported selective W deposition on Si-H vs SiO<sub>2</sub> using W ALD (SiH<sub>4</sub>/WF<sub>6</sub>). In this talk, we present co-compatible integration of TiO<sub>2</sub> ALD/ALE and W ALD for selectively patterning of TiO<sub>2</sub> films on SiO<sub>2</sub> and W films on Si-H; i.e. orthogonal TiO<sub>2</sub>/W area selective deposition on SiO<sub>2</sub>/Si-H line patterned substrates. The first ASD (TiO<sub>2</sub> ALD/ALE) selectively deposited ~18 nm TiO<sub>2</sub> film on SiO<sub>2</sub>, and the subsequent ASD (W ALD) selectively deposited ~6.1 nm W film on Si-H. Between two ASDs, intermediate HF dipping was performed to regenerate hydrogen termination on Si-H to accelerate W growth on this surface. After the orthogonal process consisting of 20 TiO<sub>2</sub> ALD/ALE supercycles and 15 W ALD cycles, TEM results show 5.3 nm TiO<sub>2</sub> on SiO<sub>2</sub> and 6.1 nm W on Si-H. During the process, W ALD simultaneously etched TiO<sub>2</sub> on SiO<sub>2</sub> while it selectively deposited W film on Si-H. More W ALD cycles in the orthogonal process showed complete removal of TiO<sub>2</sub> on SiO<sub>2</sub> and a thicker W deposition (10 nm) on Si-H. Beyond selective deposition, the results also illustrate neighboring reaction effects near region boundaries. Our findings provide an important insight into integrating two or more selective processes including ALD, ALE, CVD, and CVE for bottom-up nanofabrication.

**AP-Contributed On Demand-61 Experimental Study of Metal-Oxides Etch Selectivity, Hamid Razavi**, University of California at Los Angeles; *M. Shen, J. Hoang, T. Lill*, Lam Research Corporation; *J. Chang*, University of California at Los Angeles

Amorphous indium gallium zinc oxide (IGZO) has been attracting attentions in thin film transistors (TFTs) research as an active semiconductor channel layer due to its high transparency, high carrier mobility, and low processing temperature. In most InGaZnO (IGZO) transistors and display cells, metal-oxide etch selectivity is crucially important during the structural patterning processes in order to realize the device fabrication.

In this work, we first discuss the wet-etch selectivity of metal-oxide thin films such as Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and InGaZnO (IGZO) using different reactive solutions. Acetylacetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>), formic acid (HCOOH), and SC1 (NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/DI) were examined. The metal oxide etch rates were determined by optical ellipsometry, scanning electron microscopy (SEM), and the composition of the processed surfaces was quantified by x-ray photoelectron spectroscopy. The result suggests that IGZO was etched by formic acid preferentially at ~25:1 and ~5:1 over HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively. HAcac etches HfO<sub>2</sub> faster than Al<sub>2</sub>O<sub>3</sub> or IGZO with a ratio of ~5:1. SC1 etches Al<sub>2</sub>O<sub>3</sub> rapidly at a ratio of >100:1 over HfO<sub>2</sub> and ~20:1 over IGZO, respectively.

Next, vapor-phase etch selectivity among these oxides was investigated with formic acid and acetylacetone where the effects of pressure (100 to 250 Torr) and temperature (50 to 100°C) on the etch rate and the surface composition ratio were examined. The etch rate of IGZO processed with formic acid vapor at 80°C and 250 Torr was 7 Å/min. Using a cyclic etching process with HAcac vapor at 80°C and 250 Torr and O<sub>2</sub> plasma at 500 W and 30 mTorr for 1 min resulted in the etch per cycle (EPC) of 10 Å/cycle. In both methods preferential etching of ZnO was observed.

## Atomic Scale Processing Focus Topic

### Room On Demand - Session AP-Invited On Demand

#### Atomic Scale Processing Invited On Demand Session

**AP-Invited On Demand-1 In-situ Characterization of the Earliest Stages of Selective ALD Growth and Inhibition, Alex Martinson**, Argonne National Laboratory

**INVITED**

A vast literature of ALD synthesis and processing has been developed to produce high quality thin films with compositions that span the periodic table. However, these synthesis and processing conditions are often optimized for *adding thickness* to growing film front via (A-B)<sub>n</sub> cycles. Our associated mechanistic understanding of these processes is often gleaned from in situ study of film growth, which can be examined in detail and averaged over many sequential and identical cycles. In contrast, the earliest stages of nucleation, inhibition, and selective ALD may differ significantly with each cycle and add material with far sub-monolayer coverage. This makes characterizing and understanding nucleation, inhibition, and selective growth especially challenging. I will describe our recent efforts to understand nucleation and inhibition on a variety of substrates including self-assembled monolayers (SAMs) and graphene. A combination of in situ quartz crystal microbalance, spectroscopic ellipsometry, ab initio computation, and microcalorimetry reveal new insight into the earliest stages of deposition.

**AP-Invited On Demand-7 Atomic Layer Processing Using Low-Energy Cluster Beam Irradiation, Noriaki Toyoda**, University of Hyogo, Japan; *K. Uematsu*, University of Hyogo, Japan, Afghanistan

**INVITED**

Gas cluster ion beams (GCIBs) are clusters of several thousands of gaseous atoms or molecules. Since thousands of low-energy (several eV) molecules bombard the same position simultaneously, bombarded area experiences transient high-temperature and high-pressure conditions. These phenomena enhance surface reactions, and also enhances desorption of etching products.

We have been studying atomic layer etching using low-energy GCIB to enhance the surface reactions between adsorbed molecules and target atoms.

In this study, we report the surface reactions between metals (such as Ni) and diketone molecules induced by Ar or O<sub>2</sub>-GCIB irradiation. From the in-situ XPS studies, the nickel oxide layer with acac or hfac adsorption are selectively removed by 5 keV Ar-GCIB irradiation. After removal of the nickel oxide, metallic nickel surface appeared, and etching stopped. From the etching depth measurement after multi-cycle ALE of Ni films, it also showed that both oxidation of nickel and adsorption of acac were necessary for Ni ALE with GCIB. In this report, preliminary results of etching of MoS<sub>2</sub> using GCIB will be also reported.

**AP-Invited On Demand-13 The Thinner, The Better - Characterization of Ultra-thin Films by Low Energy Ion Scattering (LEIS), Thomas Grehl, P. Brüner**, IONTOF GmbH, Germany

**INVITED**

Current and future thin film processes require quantitative characterization from the early phases of film growth to complex film stacks with a total thickness of only a few nm. While many surface analytical techniques are challenged by this requirement, Low Energy Ion Scattering (LEIS) analysis is ideally suited for ultra-thin film and sub-monolayer characterization. The key property is its single atomic layer information depth.

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring the surface composition.

In addition to the surface composition, also the distribution of elements over the first few nm of the sample is contained in the spectra. The so-called "in-depth information" is acquired in a virtually non-destructive way, avoiding sputtering and therefore the long measurement times and artefacts associated with it. For sufficiently thin films, the depth resolution is only a few Angstroms. This allows to study the development of the film thickness while also monitoring the film closure to determine the growth mode.

In some cases, low energy noble gas sputtering can be applied to extend the depth range beyond a few nm or to handle complex materials where "in-depth" and surface information cannot be deconvoluted.

In this contribution, we will highlight a number of examples from quite different materials and film systems. These will be used to illustrate how LEIS is applied in practical way. We will show how LEIS contributes unique information for modern ultra-thin film characterization.

**AP-Invited On Demand-19 Spectroscopic Ellipsometry for Atomic Scale Processing, Harm Knoops**, Oxford Instruments Plasma Technology, Netherlands

**INVITED**

To develop, improve and understand atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) it is important to have sensitive techniques to characterize thin material increases, decreases or property changes. Spectroscopic ellipsometry (SE) is excellent for this purpose since it is a non-invasive all-optical diagnostic which can relatively easily monitor changes in thickness ranging from 0.1 to 100 nm.<sup>1</sup> This talk will discuss the relevant basics of SE and will use examples to illustrate why SE it is well suited for atomic scale processing now and in the future. Key characteristics of ALD and ALE are self-limiting behavior and synergy (needing both reaction steps to take place). Using ex situ analysis of thick films to study these aspects is cumbersome, while with in situ SE there are many examples of easy characterization. Furthermore, initial growth effects relevant in ALD and area-selective ALD are best studied in situ.

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For ALD, highlighted examples will include studying saturation, which can provide evidence for important processes such as the redeposition effect for silicon nitride ALD,<sup>2</sup> and studying saturation is even possible for 2D materials which are challenging to model by SE. When using ex situ SE and data by other diagnostics (e.g. electrical and infrared) a deeper investigation of material properties is possible. For instance electrical properties can be calculated from the Drude absorption yielding insight into the electrical resistivity and electron scattering effects in ultrathin ZnO films.<sup>3</sup> For ALE, SE has been much less used than for ALD, but similarly there are great opportunities and examples there. Easiest analysis occurs when smooth films of the target material are available (or deposited) on substrates. To this end the synergy of ALE has been tested and confirmed for ALE of ZnO using H<sub>2</sub> and O<sub>2</sub> plasma.<sup>4</sup> But also recently for ALE of Al<sub>2</sub>O<sub>3</sub> using AlMe<sub>3</sub> and SF<sub>6</sub>.<sup>5</sup> Note that the latter chemistry can also result in the ALD of AlF<sub>3</sub> and SE is a powerful tool to determine in situ whether ALD or ALE is occurring and under which circumstances. By clever set up and utilization of this diagnostic, SE has become a powerful and often essential tool to develop and understand ALD and ALE processes.

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<sup>3</sup> Knoops et al., JVST A 33, 021509 (2015)

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<sup>5</sup> Chittock et al., *In preparation*

**AP-Invited On Demand-25 Area-selective Atomic Layer Deposition of Palladium and Atomic Layer Etching of Palladium, H. Nallan, X. Yang, B. Coffey, John Ekerdt, University of Texas at Austin**

**INVITED**

ALD of metals can suffer from long nucleation delays leading to unwanted growth outside the patterned regions. We present an approach that first deposits a metal oxide selectively and reduces this metal oxide to the metal. This metal then serves as the nucleation site for ALD of Pd using a precursor chemistry that requires activation of molecular hydrogen. In the event non-selective nucleation occurs on passivated regions, we describe a low temperature ALE route to etch clusters/islands on the passivated regions faster than the desired film. This low temperature route exploits the general findings that metal oxides can be etched by a variety of vapor phase etchants – the issue is controlled oxidation while minimizing damage to adjacent surfaces. We present a low temperature route that involves VUV activation of O<sub>2</sub> to produce atomic oxygen and ozone, with atomic oxygen being the dominant species that oxidizes the near surface region of Pd. Oxidation extents differ between continuous films and discontinuous films enabling the removal of metal islands without significantly etching the film.

This talk will discuss patterning an oxide substrate using UV-crosslinked 40-nm polystyrene (PS) films; the uncrosslinked PS is dissolved with toluene to expose the oxide surface. The ALD of NiO is highly selective on the exposed oxide surface using bis(N,N'-di-tert-butylacetamidino)nickel(II) and H<sub>2</sub>O as coreactants. Ni and partially reduced NiO(1-x) are generated using molecular hydrogen and/or atomic hydrogen to present a surface that dissociates H<sub>2</sub> and enables Pd ALD with Pd(hfac)<sub>2</sub> and H<sub>2</sub> to proceed with little to no nucleation delay. Finally, the talk will discuss vacuum ultraviolet (115 nm < λ < 400 nm) enhanced atomic layer etching (ALE) of thin (~2 and 20 nm) Pd films at 100 °C using formic acid as the etchant. Density functional theory is used to study the adsorption of oxidants (O and O<sub>3</sub>) and nudged elastic band calculations describe O diffusion into the films to understand the kinetic limitations of the oxidation step. Low-temperature Pd oxidation at 100 °C is achieved by exposure to vacuum ultraviolet (VUV) light (λ < 160 nm) in the presence of O<sub>2</sub>. The islands are completely oxidized while Pd oxidation of a film is limited to approximately one atomic layer. Any PdO that forms is etched by exposure to formic acid.

**AP-Invited On Demand-31 Strategies for a Selective Deposition Process Combining Deposition and Etching Steps in a Unique Tool, Christophe Vallée, SUNY POLY, Albany; M. Bonvalot, T. Yeghoyan, R. Vallat, M. Jaffal, V. Pesce, LTM - UGA/CNRS, France; A. Chaker, University of Manchester, UK; S. Belahcen, G. Lefevre, B. Pellissier, LTM - UGA/CNRS, France; N. Possémé, R. Gassilloud, CEA/LETI-University Grenoble Alpes, France**

**INVITED**

Selective deposition by ALD can be obtained using: inherent selectivity of the process<sup>1-2</sup>, surface activation<sup>3</sup>, surface deactivation<sup>4-5</sup>, and ABC typesuper-cycles<sup>6</sup>. The strategy developed in our laboratory is based on super-cycles with alternate deposition and etching steps<sup>7-10</sup> in a unique ALD tool.

Up to now, we have developed ASD processes with many different types of etching steps, such as high-pressure plasma etching (radicals only), Reactive Ion etching, Atomic layer etching or sputtering (physical) etching steps. For this purpose, two different PEALD tools are used: either a CCP capacitive discharge tool from Kobus (now Plasma-Therm) with a grounded substrate holder, or an ICP PEALD tool from Oxford (Flexal) with an additional RF biasing of the substrate.

Plasmas from the PEALD tool can also be developed to the benefit for ASD processes. For instance, an appropriate plasma chemistry can modify the nucleation delay. Moreover, thanks to substrate biasing, one can also take advantage of energetic ions from the plasma to locally modify the nucleation delay as well as the materials GPC or density. This latest route combined with a post-deposition etching process is a fast and easy to develop process for topographically selective deposition (deposition in one space direction only).

This presentation will outline and provide several examples of all these different scenarios that we have developed recently in our group, as well as state of the art ASD solutions from other groups using etching steps or ions in PEALD processes.

<sup>1</sup>K. J. Hughes and J.R. Engstrom, J. Vac. Sci. Technol. A **30**, 01A102 (2012)

<sup>2</sup>S. E. Atanasov et al, J. Vac. Sci. Technol. A **34**, 01A148 (2016)

<sup>3</sup>A.J. M. Mackus et al, Chem. Mater. **24**, 1752 (2012)

<sup>4</sup>M. Fang and J.C. Ho, ACS Nano **9**, 8651 (2015)

<sup>5</sup>E. Farm et al, Sci. Tech. **27**, 074004 (2012)

<sup>6</sup>A. Mameli et al, ACS Nano **11**, 9303 (2017)

<sup>7</sup>R. Vallat et al, J. Vac. Sci. Technol. A **35**, 01B104 (2016)

<sup>8</sup>R. Vallat et al, J. Vac. Sci. Technol. A **37**, 020918 (2019)

<sup>9</sup>A. Chaker et al, Appl. Phys. Lett. **114**, 043101 (2019)

<sup>10</sup>C. Vallée et al, J. Vac. Sci. Technol. A **38**, 033007 (2020)

**AP-Invited On Demand-37 Thermal Atomic Layer Etching - An Emerging and Enabling Etching Technology, Andreas Fischer, A. Routzahn, R. Gasvoda, P. Lemaire, J. Sims, T. Lill, Lam Research Corporation**

**INVITED**

In this presentation we discuss the state-of-the-art status of thermal atomic layer etching of various materials such as metals, metal oxides, metal nitrides, semiconductors and their oxides. We outline the basic chemical and thermodynamic reaction principles and identify materials relevant to the semiconductor industry that lend themselves for isotropic atomic layer etching.

Furthermore, application examples of this new etch technology are illustrated on device structures and its benefits as well as challenges are examined. We give an example of the technical challenges related to high aspect-ratio atomic layer etching including an overview on how to mitigate it in modern 3D NAND test structures.

Finally, we provide an outlook of the role thermal ALE can play in the manufacturing of advanced semiconductor devices.

**AP-Invited On Demand-43 Nanoscale Chemical Analysis and Mapping of Atomic Scale Processes via Photo-Induced Force Microscopy, Sung Park, D. Nowak, T. Albrecht, Molecular Vista**

**INVITED**

As device feature sizes move beyond sub-7 nm technology node, atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) are being adopted to gain control over key processing parameters. These techniques are commonly combined with thin polymer barrier layers such as self-assembled monolayers (SAM) that are selectively located to achieve area selective deposition or etching. Atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials demand new metrology and

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characterization techniques to be developed to adequately assess and monitor these advanced processing techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-10 nm spatial resolution). The spectroscopic capability is useful for ascertaining the quality of the molecular species while the mapping capability is useful for investigating chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, sequential infiltration synthesis, and a variety of area-selective deposition techniques. PiFM applications on various atomic scale processes will be presented.

[1] D. Nowak et al., *Sci. Adv.* 2, e150157 (2016).



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