Thin Films Division
Room 104B - Session TF+PS-TuA

Atomic Layer Processing: Chemistry & Surface Reactions for Atomic Layer Processing

Moderators: Jessica Kachian, Intel Corporation, Keren Kanarik, Lam Research Corporation

2:20pm **TF+PS-TuA-1 N-heterocyclic Carbenes on Au and Cu Surfaces*, Cathleen Crudden,*** Queen's University, Canada **INVITED**

N-Heterocyclic carbenes (NHCs) are an exciting new class of ligand for metal surfaces, with potentially interesting applications in patterning and surface functionalization. In this talk, we will address the use of NHCs as ligands for various metal surfaces including coinage and other metals. The functionalization of flat and structured surfaces will be presented and potential applications in etching.

3:00pm **TF+PS-TuA-3 Enhancing Nucleation in Platinum Atomic Layer Deposition by Surface Pre-Treatment with Small Organometallic Molecules*, Camila de Paula,*** *L Zeng, S Bent,* Stanford University

Pt thin films have a wide variety of applications in microelectronics, catalysis, and energy technologies. Since most of these applications require a conformal and pinhole-free thin film, achieving good nucleation is an important requirement. It is believed that a low abundance of dissociated oxygen atoms in the initial stages of the Pt ALD process leads to a nucleation delay and island growth. The nucleation and growth mechanisms have a big impact on the properties of the resulting thin film. If nucleation is inhibited, isolated particles rather than a continuous film may be deposited at low cycle numbers (island-growth), whereas if nucleation is facile, a continuous film may be formed at much lower thicknesses.

While there have been studies focused on the surface reactions that occur during Pt ALD, there is still a lack of understanding of how the substrate surface properties affect nucleation in the initial stages of ALD. There have been reports of methods aimed at enhancing nucleation for specific substrates, such as using a wet piranha etch on silicon substrates. Other studies have used high surface energy adhesion layers, such as W, in order to overcome the nucleation delay.

The goal of this study is to develop a surface pre-treatment technique that enhances Pt ALD nucleation independent of substrate choice, while inducing minimum surface modification of the substrate. In this work, the influence of a sub-monolayer surface coverage of small organometallic molecules on the nucleation and growth of Pt by ALD was studied. It was observed that introducing a short pulse of dimethylaluminum chloride (DMACl) prior to Pt deposition leads to the formation of a continuous film after fewer than 100 cycles on thermally grown silicon oxide vs. over 200 cycles on a non-treated sample. Scanning electron microscopy (SEM), synchrotron based grazing incidence small angle X-ray scattering (GISAXS) and X-ray photoelectron spectroscopy (XPS) were used to analyze the ALD growth mechanism on various treated and untreated substrates. The formation of densely-packed large Pt nanoparticles was observed on the treated surface. GISAXS analysis of the Yoneda-Peak position and pattern showed that the surface treatment leads to nanoparticle coalescence in the very early stages of ALD. Interestingly, a comparison of DMACl to other small organometallic molecules showed that some molecules induced the opposite behavior, instead leading to inhibited Pt ALD. The detailed growth mechanism and possible reaction pathways leading to these results will be discussed.

3:20pm **TF+PS-TuA-4 Mass Spectrometer Studies of Volatile Etch Products Produced by Ligand-Exchange Reactions During Thermal Atomic Layer Etching*, Joel Clancey,*** *A Cavanagh, S George,* University of Colorado Boulder

Atomic layer etching (ALE) using sequential, self-limiting surface reactions is an important technique for removing material with atomic layer control. In addition, selective ALE is required for the maskless fabrication of advanced devices as feature sizes become smaller than available lithography. This study reports the study of volatile etch products produced by ligand-exchange reactions during thermal ALE and develops our understanding of selective thermal ALE.

Previous studies have revealed selective thermal ALE in the etching of Al_2O_3, ZrO_2 and HfO_2 using fluorination and ligand-exchange reactions [1]. In this work, we used metal fluoride powders to study volatile etch products produced by fluorination and ligand-exchange reactions during thermal ALE. An *in situ* quadrupole mass spectrometer (QMS) was employed to characterize the etch products produced during the thermal etching of AlF_3, ZrF_4 and HfF_4 powders between 200°C and 300°C using TMA, DMAC, $SiCl_4$ and $TiCl_4$ as the metal precursors.

Thermal Al_2O_3 ALE occurs using HF and TMA as the precursors [2]. For the reaction of TMA with AlF_3 powders, the observed etch products are dimers such as $[AlF(CH_3)_2]_2$ and $[AlF(CH_3)_2\text{-}Al(CH_3)_3]_2$. These products are equivalent to the dimer etch products observed earlier for the reaction of TMA with fluorinated Al_2O_3 during thermal Al_2O_3 ALE. In contrast, Al_2O_3 ALE does not occur with either $SiCl_4$ or $TiCl_4$ as the metal precursors [1]. For the reaction of $SiCl_4$ and $TiCl_4$ with AlF_3 powders, the observed reaction products are $SiFCl_3$ and $TiFCl_3$, respectively. There is halide-exchange between the $SiCl_4$ and $TiCl_4$ metal precursors and the AlF_3 surface. However, there is no observation of volatile Al-containing products that would be consistent with Al_2O_3 etching.

We are developing a matrix that correlates volatile etch or ligand-exchange products with the previous etching results. We are also using density functional theory (DFT) to predict the etch products during thermal ALE. These DFT calculations correctly predict the dimer etch products during Al_2O_3 ALE. This approach is advancing our understanding of selective thermal ALE.

[1] 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).

[2] Younghee Lee, Jaime W. DuMont and Steven M. George, “Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions”, *Chem. Mater.* **28**, 2994 (2016).

4:20pm **TF+PS-TuA-7 Beyond Conventional Lithography – Using Self-assembly to Create Patterns for New Device Fabrication Techniques*, Michael Morris,*** Trinity College Dublin, Ireland **INVITED**

The microelectronics industry is being challenged to maintain progress at a similar rate to that which has been seen for nearly 50 years. With the dissolution of the International Technology Road Map for Semiconductors (ITRS) has come the realization that scaling is not the only solution that can drive improvements in the silicon chip industry. Indeed several competing technologies may emerge in the near future including device and interconnect structures fabricated from 2D materials. At device level, feature size will probably continue to decrease as solutions for sub-10 nm nodes become available. Note that whist feature size has shrunk, gate length has not significantly decreased for several years. New device materials with higher mobilities such as 2D materials will be seen as promising but their implementation into conventional device fabrication methods remains problematical. The interconnect issue may be the most critical area for development since delay times limiting clock speed. For these reasons the integration of non-traditional active circuitry in back end of line (BEOL) processes is highly attractive to control chip processes or add function such as memory. It also allows promising materials such as 2D to be intergated at less challenging length scales.

All of these approaches and others will require innovative fabrication techniques suitable for integrating new materials, patterning them and developing function. We will centre on the use of self-assembled block copolymer films and related methods that may be able to develop device structures without expensive high resolution lithography and at low thermal budgets needed for integration of multiple device layers.

5:00pm **TF+PS-TuA-9 Calculations of Etch Products from Thermal Atomic Layer Etching Using Fluorination and Ligand-Exchange Reactions*, Andrew Cavanagh,*** *J Clancey, S Sharma, S George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 can be accomplished using sequential, self-limiting fluorination and ligand-exchange surface reactions with hydrofluoric acid (HF) and trimethyl aluminum (TMA, $Al(CH_3)_3$) as the precursors. Fluorination by HF converts the surface of Al_2O_3 to AlF_3. Ligand-exchange reactions then occur between TMA and the AlF_3 surface. The first ligand-exchange reaction is believed to be: $AlF_3(s) + Al(CH_3)_3(g) \rightarrow AlCH_3F_2(s) + Al(CH_3)_2F(g)$ where “s” indicates a surface species and “g” indicates a gas phase species. Additional ligand-exchange reactions can then react $AlF_2CH_3(s)$ to $AlF(CH_3)_2(g)$. Recent quadrupole mass spectrometry (QMS) studies have observed that the main etch products during Al_2O_3 ALE are the dimers $AlF(CH_3)_2\text{-}AlF(CH_3)_2$ and $AlF(CH_3)_2\text{-}Al(CH_3)_3$. These dimers may be formed from the monomer $AlF(CH_3)_2$ etch product pairing with itself or with the $Al(CH_3)_3$ metal precursor.

To understand these dimer etch products, density functional theory (DFT) calculations were performed on all possible dimers that could be produced from the four possible monomer species ($Al(CH_3)_3$, $Al(CH_3)_2F$, $AlCH_3F$, AlF_3). Each dimer consisted of a pair of bridging ligands between the two Al metal centers and four terminal ligands. The bridging ligands could be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges resulted in the most stable dimers while the (CH_3, CH_3) bridges resulted in the least stable dimers. In agreement with the QMS results, these DFT calculations predict that the $AlF(CH_3)_2$-$AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most viable etch product.

Additional DFT computational studies have also been performed for ligand-exchange reactions on fluorinated surfaces of Al_2O_3, ZrO_2 and Ga_2O_3 with various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. These calculations model the ligand-exchange surface reactions during Al_2O_3, ZrO_2 and Ga_2O_3 ALE. For all systems studied to date, the calculations indicate that dimer species are the preferred etch products. Future QMS experiments will observe etch products and compare with the DFT computational studies for a more complete understanding of thermal ALE.

5:20pm **TF+PS-TuA-10 Formation of Monolayers and Multilayers During the Vapor-Phase Deposition of Dodecanethiols on Copper Oxide***, **David Bergsman**, T Liu, R Closser, S Bent,* Stanford University

The deposition of alkanethiols onto copper and copper oxide has been widely studied for use in the passivation of surfaces and as ultrathin blocking layers. The formation of alkanethiol self-assembled monolayers (SAMs) on copper oxide is particularly interesting in that thiols are known to etch and reduce copper oxide surfaces before ultimately forming a SAM. This has sometimes resulted in films much thicker than expected for a monolayer, leading to the hypothesis that this etching process can create multilayers, though the structure of those multilayers and the mechanism behind their formation were not explored. In recent years, the use of SAMs to enable area-selective atomic layer deposition (ALD) for back-end semiconductor processing has created renewed interest in the study of thiol deposition onto copper, particularly through vapor-phase approaches that can be more easily incorporated into industrial semiconductor fabrication processes. However, no studies have reported the formation of Cu-thiolate multilayers through the vapor-phase.

In this work, we examine the vapor deposition of dodecanethiols (DDTs) onto copper and copper oxide surfaces. We show using atomic force microscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy/electron energy loss spectroscopy that this deposition onto copper oxide surfaces results in the formation of up to 8 nm thick Cu-thiolate multilayer films, rather than SAMs. In contrast, pre-removal of the copper oxide and subsequent DDT exposure creates 2 nm thick SAMs, suggesting that the etching of the copper oxide films by thiol molecules is a key step in the multilayer formation. Synchrotron-based grazing-incidence X-ray diffraction shows these thick films to be highly crystalline, with bilayer thiol structures sandwiched between layers of copper atoms. Crystallites are shown to be oriented both perpendicular and parallel to the surface. We further explore the degradation of these multilayers, demonstrating with scanning electron microscopy and XPS that the films appear to dewet into micron-sized particles after exposure to air. Continued air exposure results in the oxidation of the sulfur and copper in the films on a time scale consistent with DDT monolayers. Finally, the implications of this multilayer formation on area-selective ALD will be discussed.

5:40pm **TF+PS-TuA-11 Exchange Reactions During Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum***, **Tyler Myers**, A Cano, J Clancey, D Lancaster, S George,* University of Colorado at Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 150-250°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with Zn-CH_3CH_3 species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

6:00pm **TF+PS-TuA-12 3D Feature Profile Simulation Coupled with Realistic Plasma Surface Reaction Model for ALE Process***, Y Im, **YeongGeun Yook**, H You, J Park,* Chonbuk National University, Republic of Korea*; D You,* KW Tech, Republic of Korea*; K Choi,* Chonbuk National University, Republic of Korea*; W Chang,* National Fusion Research Institute, Republic of Korea

Recently, atomic layer etching (ALE) processes have attracted much interest for sub-10nm semiconductor fabrication process. Notably, a cyclic plasma-enhanced fluorocarbon ALE process using the conventional plasma etch tools has investigated for its selective etching and atomic-level control. In spite of its superior merits, the detailed studies remain to apply sub-10nm 3D nanoscale feature patterns due to its complexity. To address this issue, we developed a 3D feature profile simulator which was composed of a Zero-D bulk plasma simulator, a multiple-level set moving algorithm based on a hash map, a GPU based ballistic transport algorithm, and a surface reaction model. In this work, we focus on the development of a transient surface reaction model of ALE process to capture the realistic surface reaction. Finally, 3D feature profile simulations coupled with the surface reaction model were verified with experimental data. We believe that this approach enables us to understand unveiled phenomena of ALE process.

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