Atomic Layer Etching
Room Baekeland - Session ALE1-MoA
Thermal and/or Isotropic ALE II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Adrie Mackus, Eindhoven University, Netherlands

1:30pm **ALE1-MoA-1 Chlorination and Ligand Addition for Thermal ALE of Metals***, **Jessica Murdzek**,* University of Colorado Boulder*; A. Lii-Rosales,* Lam Research Corp*; S. George,* University of Colorado Boulder **INVITED**

Thermal atomic layer etching (ALE) is defined by sequential surface modification and volatile release reactions. Thermal ALE of metals 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 oxidizing the metal via chlorination using SO_2Cl_2. Subsequently, the metal is etched by addition of an L ligand to the metal center to create a stable, volatile etch product, MCl_xL_y (Figure 1). The L ligands explored in this work were PMe_3 and tetramethylethylenediamine (TMEDA).

The chlorination and ligand-addition approach for metal ALE is based on the Covalent Bond Classification (CBC) method. X ligands are one-electron donors like Cl and other halogens. L ligands are two-electron donors like PMe_3. TMEDA is a bidentate ligand.One TMEDA ligand acts as two L ligands since TMEDA binds to the metal center through the lone electron pairs on the two nitrogen groups.According to the CBC method, nickel complexes typically have NiX_2L_3 or NiX_2L_2 configurations.Likewise, cobalt complexes are typically found in the CoX_2L_4, CoX_2L_2, or CoX_3L_3 configurations. The goal for Ni or Co ALE is to create these volatile metal compounds using sequential SO_2Cl_2 and L ligand surface reactions.

Both Ni and Co ALE have been studied with in situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) to determine etch rate.Quadrupole mass spectrometry (QMS) was also employed to determine the volatile metal-containing etch species. Using SO_2Cl_2 and PMe_3, Ni etch rates varied from 0.1-3 Å/cycle at temperatures from 75-200 °C.QMS measurements also identified $NiCl_2(PMe_3)_2$ (NiX_2L_2) as the stable volatile etch product.Cobalt ALE using SO_2Cl_2 and TMEDA displayed etch rates from 1-12 Å/cycle at temperatures from 175-300 °C (Figure 2). QMS measurements also detected $CoCl_2$(TMEDA) (CoX_2L_2) as the stable volatile etch product.In addition, cobalt can be etched using SO_2Cl_2 and PMe_3 from 70-200 °C, with etch rates between 2-4 Å/cycle. These two Co ALE pathways are complementary with TMEDA useful at higher temperatures and PMe_3 useful at lower temperatures.

Many other X and L ligands could define additional halogenation and ligand-addition reactions.Using the CBC method as a guide, this strategy should lead to the development of various other metal ALE processes.

2:00pm **ALE1-MoA-3 Thermal ALE of Molybdenum via Low Temperature Oxidation in Ozone and Wet Chemical Oxide Dissolution***, **Antoine Pacco**,* IMEC, Belgium*; N. Teppei, S. Iwahata, A. Iwasaki,* SCREEN, Japan*; E. Altamirano Sanchzez,* IMEC, Belgium

Over the last decade, isotropic metal recess has received increased attention due to its relevance for both logic and memory applications. Controllable partial recess of metal requires a high level of accuracy, uniformity, and selectivity. In this work, we present atomic layer etching (ALE) of Mo for its application for Mo recess in buried power rail (BPR) [1] and 3D-NAND structures. Given its improved conductivity at sub 20 nm dimensions, Mo could be a possible candidate to replace W [2].

ALE of Mo thin films was achieved using a sequential oxidation in ozone gas followed by the removal of the molybdenum oxide by simple wet chemical etching. Oxidation in ozone gas has a lower activation energy than in oxygen, thereby effectively reducing the temperature budget of the etching process. We found that the molybdenum oxide formed during oxidation was MoO_3. This Mo (VI) oxide is easier to dissolve in aqueous alkaline solutions than WO_3 which has very low solubility in aqueous solutions [3] and requires more complex removal mechanisms [4-5]. Finally, the underlying Mo metal was unaffected in the aqueous alkaline solutions used allowing for a *selective* removal of MoO_3 as required by an ALE method.

Recess of blanket films as well as patterned samples was studied using this cyclic process and the etch per cycle (EPC) was increased by increasing the oxidation temperature. We were able to tune the EPC between 2 and 6 nm by increasing the substrate temperatures from 180 to 290 °C. No significant differences in EPC were observed between the recess of Mo metal deposited by either plasma vapor deposition (PVD) or atomic layer deposition (ALD). The effect of an annealing step on recess amount was also investigated. Ultimately, roughening of the surface, a typical unwanted effect from conventional *continuous* wet etching of polycrystalline materials [6], was mitigated by this method.

We found that the thermal-wet ALE presented here is capable of recessing Mo isotropically and selectively towards a broad range of materials (Si, SiO_2, SiN, Al_2O_3, ...). Therefore, applications such as next-generation interconnects, BPR and 3D-NAND memory devices could benefit from this cyclic recess etch method.

[1] A. Gupta et al., Buried Power Rail Metal exploration towards the 1 nm Node, IEDM 2021

[2] D. Gall, J. Appl. Phys. 127, 050901, 2020.

[3] M. Anik and T. Cansizoglu, J. Appl. Electrochem. 36, 603–608, 2006.

[4] W. Xie and G. N. Parsons, J. Vac. Sci. Technol. A 38, 022605, 2020.

[5] N. R. Johnson and S. M. George, ACS Appl. Mater. Interfaces, 9, 34435−34447, 2017.

[6] A. Pacco, Y. Akanishi, Q. T. Le, Solid State Phenomena 314, 295-301, 2021.

2:15pm **ALE1-MoA-4 Selective Thermal Atomic Layer Etching of CoFeB Over MgO by Sequential Exposure to Chlorine and Diketone***, M. Konh, **Andrew V. Teplyakov**,* University of Delaware

Thermal atomic layer etching (ALE) is one of the most promising methods to have precise control of the thin film thickness is required for fabrication of microelectronic devices. CoFeB alloy films are commonly used as ferromagnetic layers in magnetic tunnel junction for integrated memory devices, where they are usually separated by an insulating barrier layer such as MgO. It is important to have a method that can selectively reduce the thickness of CoFeB alloy thin film without affecting MgO layer. Here, selective thermal atomic layer etching of CoFeB alloy thin film using sequential exposure to chlorine and acetylacetone (acacH) is investigated. During the ALE process the concentration of each element in the alloy remains constant according to the X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) is used to indicate the surface morphology preservation after the ALE process. The changes in thickness following thermal ALE on the patterned samples are recorded by AFM to deduce the etch rate, and to evaluate the ALE process on MgO patterns deposited on top of the CoFeB alloy films. To uncover the molecular mechanism of the ALE process, temperature programmed desorption (TPD) experiments are performed to detect possible key desorbing fragments.

2:30pm **ALE1-MoA-5 Ligand-Exchange and Etching Reactions between Metal Fluorides and Silane Precursors Containing Different Ligands***, A. Lii-Rosales, V. Johnson, A. Cavanagh,* University of Colorado Boulder*; A. Fischer, T. Lill,* Lam Research Corporation*; S. Sharma, **Steven George**,* University of Colorado Boulder

Metal fluorides can be spontaneously etched by ligand-exchange reactions. During these reactions, the exchange of ligands between the incoming precursor and the metal fluoride leads to the volatilization of the metal fluoride. These ligand-exchange reactions are important in many thermal atomic layer etching (ALE) processes. To test the effectiveness of different ligands for ligand exchange, the spontaneous etching of metal fluorides by silane precursors containing different ligands was investigated using *in situ* quadrupole mass spectrometry (QMS). The metal fluorides were GaF_3, InF_3, ZnF_2, ZrF_4, HfF_4, and SnF_4. The silane precursors were $SiCl_4$, $SiCl_2(CH_3)_2$, $SiCl(CH_3)_2H$, and $Si(CH_3)_4$. These silane precursors provide Cl, CH_3 or H ligands for the ligand-exchange reaction.

The QMS results showed that F/Cl ligand exchange was observed for all the metal fluorides with the chlorine-containing silane precursors. In addition, all the volatile metal etch products were metal chlorides, namely $GaCl_3$, $InCl_3$, $ZnCl_2$, $ZrCl_4$, $HfCl_4$, and $SnCl_4$. Results for $SiCl_2(CH_3)_2$ on GaF_3 are shown in Figure 1. No metal methyl complexes were detected as volatile metal etch products indicating no F/CH_3 exchange. For $SiCl(CH_3)_2H$ as the silane precursor, the observation of $SiF_2(CH_3)_2$ indicated that F/H exchange is also possible in addition to F/Cl exchange. For the various metal fluorides, the dominance of F/Cl exchange led to nearly equivalent onset temperatures for ligand exchange and for etching to yield metal chlorides as displayed in Figure 2.

Thermochemical calculations of the ligand-exchange reactions verified the formation of metal chlorides. All F/Cl exchanges were thermodynamically favorable as demonstrated by the negative changes in Gibbs free energy (ΔG). These experimental and theoretical results provide guidelines for designing thermal ALE processes. After the fluorination reaction to produce metal fluorides during thermal ALE, ligand-exchange reactions using Cl-containing silane precursors should be effective for etching if the metal fluoride has corresponding volatile and stable metal chlorides.

2:45pm **ALE1-MoA-6 Thermal Atomic Layer Etching of Zinc Sulfide (ZnS) Using Sequential Al(CH_3)$_3$ and HF Exposures***, Taewook Nam***, *J. Partridge, J. Murdzek, S. George,* University of Colorado Boulder

Thermal atomic layer etching (ALE) processes have been developed from many materials including various oxides, nitrides and metals. This study introduces the thermal ALE of a sulfide material - zinc sulfide (ZnS). ZnS thermal ALE was demonstrated using trimethylaluminum ($Al(CH_3)_3$, TMA) and hydrogen fluoride (HF) as the reactants at temperatures from 225 to 300°C. The ALE was performed on ZnS atomic layer deposition (ALD) films that were deposited using diethylzinc ($Zn(C_2H_5)_2$, DEZ) and hydrogen sulfide (H_2S) as the precursors on p-type Si wafers at growth temperatures from 100 to 300°C. The etch rates were determined by monitoring the thickness of the ZnS ALD films using in-situ spectroscopic ellipsometry. Quadruple mass spectroscopy (QMS) was also used to detect the volatile etch products during ZnS thermal ALE to determine the ALE mechanism.

For the ZnS ALD films grown at 100°C, the etch rate varied from 1.4 Å/cycle at 225°C to 2.2 Å/cycle at 300°C. For the ZnS ALD films grown at 300°C, the etch rate was slightly lower and varied from 0.8 Å/cycle at 225 °C to 1.9 Å/cycle at 300°C. The ZnS ALD films grown at 300°C may have slightly higher densities that slow the etch rate. The ZnS ALD films were amorphous according to X-ray diffraction analysis. However, for the ZnS ALD films grown at 300°C, small islands remained on the surface after most of the ZnS ALD film was etched away. After the ZnS thermal ALE, these islands were confirmed as crystalline ZnS particles by XRD.

QMS analysis of the volatile etch products resulting from the sequential $Al(CH_3)_3$ and HF exposures revealed evidence for a conversion mechanism for ZnS thermal ALE as shown in Figure 1. During this conversion mechanism, $Al(CH_3)_3$ converts the top of the ZnS film to an Al_2S_3 surface layer and releases $Zn(CH_3)_2$ as the volatile product. Subsequently, HF fluorinates the Al_2S_3 layer to AlF_3 and releases H_2S as the volatile product. Then $Al(CH_3)_3$ removes the AlF_3 layer by ligand-exchange and also converts more ZnS to Al_2S_3. These reactions release various $AlF(CH_3)_2$ dimers and trimers from ligand-exchange and $Zn(CH_3)_2$ from the conversion. The volatile products measured by QMS during several sequential $Al(CH_3)_3$ and HF exposures are displayed in Figure 2.

3:00pm **ALE1-MoA-7 Requirements Beyond Etch Per Cycle for Thermal ALE in Semiconductor Manufacturing***, Martin McBriarty,* EMD Electronics

Isotropic ALE is poised to enter high volume manufacturing (HVM) of semiconductor devices within this decade. Several new process steps enabling more complex logic and memory architectures will incorporate ALE chemistries derived from fundamental research in academic and industrial R&D labs. The rigorous requirements of HVM introduce significant challenges for ALE integration, such as high selectivity, good process control in high aspect ratio features, and extremely low levels of contaminants and residues. Safety and sustainability are also key concerns, as ALE reagents and byproducts are often corrosive, toxic, or have high global warming potential. The choice of candidate chemistries and types of laboratory experiments at the early stages of ALE research can help identify processes which can be more seamlessly integrated into HVM. This presentation aims to clarify some of the semiconductor industry's pressing ALE needs beyond a good etch per cycle, with recommendations for how researchers can strengthen the impact of ALE experiments.

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