Atomic Layer Etching
Room Grand Ballroom H-K - Session ALE-MoA

Metal ALE

Moderators: Dr. Thorsten Lill, Lam Research Corporation, Dr. Tristan Tronic, Intel Corporation

4:00pm **ALE-MoA-11 Wet Atomic Layer Etching of Metals*, Paul Abel,*** Tokyo Electron America, Inc. **INVITED**

Here we present a new strategy for implementing atomic layer etching (ALE) of metals using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through dissolution of the self-limiting passivation layer rather than volatilization. This relaxes the temperature requirements of thermal ALE, and the sputter threshold requirements for plasma ALE. Solubility is strongly dependent on solvent species, so solvent exchange can be used as the trigger for release of the self-limiting passivation layer as an alternative to ligand exchange. In the first half of the etch cycle, a self-limiting metal-ligand surface complex is formed on exposure to the first etch solution. The surface layer must be insoluble in this solution, but readily soluble in the second etch solution in order to complete the ALE cycle. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is required for material removal. A diagram of this wet ALE process is shown in Figure 1.

Most transition metal complexes form around oxidized metal centers, so formation of the surface complex is governed by solution redox chemistry in the presence of appropriate ligands. Solubilization of this complex can be achieved in one of several ways. Solvent exchange can be used to dissolve the layer in an appropriate solvent. Ligand exchange in a non-redox active solution can be used to alter the solubility of the surface complex without changing the solvent or reacting with the underlying substrate. And lastly, ion exchange can be used if the surface complex is a coordination compound containing both a ligand-bound complex ion and a counterion.

In this talk, we apply these strategies to the wet ALE of copper and cobalt. These metals easily form thick native oxide layers. The thickness of this layer, as well as the ease with which it forms makes it inappropriate to use as the modified layer for wet ALE. Exposure to an appropriate ligand-containing solution, however, forms a monolayer of metal-ligand complex on the native oxide surface. This metal-ligand complex is a much more appropriate modified layer, and the etch amount per cycle is strongly dependent on ligand chemistry. Both ligand surface packing density and ligand binding strength influence the metal removal rate. Selective removal can then be accomplished through either a solvent exchange to directly dissolve the modified layer or a ligand exchange to form a more soluble compound through reactive dissolution.

4:30pm **ALE-MoA-13 Thermal Atomic Layer Etching of Molybdenum Based on Sequential Oxidation and Chlorination Reactions*, Taewook Nam,*** *J. Partridge, S. George,* University of Colorado at Boulder

Previous pathways for thermal ALE of metals, such as Cu and Co, have employed either oxidation or chlorination reactions for surface modification followed by either ligand-substitution or ligand-addition reactions for volatile release. This study introduces another mechanism for the thermal ALE of metals using sequential oxidation and chlorination reactions. This mechanism relies on the metal having volatile oxychloride complexes. The thermal ALE of Mo was studied using quartz crystal microbalance (QCM), x-ray reflectivity (XRR), and quadrupole mass spectrometry (QMS) measurements. Mo films were first deposited on quartz crystals or silicon coupons using sputtering. The mass or thickness changes were then measured versus sequential oxidation and chlorination reactions using O_3/O_2 and $SOCl_2$ as the reactants.

The QCM measurements observed very digital mass changes during the sequential O_3/O_2 and $SOCl_2$ exposures. QCM results showed pronounced mass gains during O_3/O_2 exposures and distinct mass losses during $SOCl_2$ exposures. QCM measurements for three cycles of Mo ALE at 175°C are displayed in Figure 1. The mass changes were also self-limiting versus O_3/O_2 and $SOCl_2$ reactant exposure. The mass loss per Mo ALE cycle was -1,600 ng/cm^2 or 15.7 Å/cycle under the saturation reaction conditions at 175°C. The Mo ALE etch rate was studied from 100°C to 250°C and larger etch rates were observed at higher temperatures.

Mo ALE is dependent on the release of volatile oxychloride etch products. For under-saturation reaction conditions, the mass changes during the O_3/O_2 exposures could either be negative or positive. Lower O_3/O_2 exposures led to negative mass changes and higher O_3/O_2 exposures led to positive mass changes. This behavior can be explained based on the volatile oxychloride etch product during Mo thermal ALE. There is chlorine on the surface after the $SOCl_2$ exposure. Initial O_3/O_2 exposures remove the chlorine as a volatile Mo oxychloride product and produce a mass loss. As the chlorine is removed, larger O_3/O_2 exposures can then proceed to oxidize the Mo surface and produce a mass gain.

QMS experiments were performed to identify the etch products. To improve the detection sensitivity, these experiments utilized various powder samples to model the Mo surface after the O_3/O_2 or $SOCl_2$ exposures. The main Mo oxychloride species detected was MoO_2Cl_2. Figure 2 shows the observation of MoO_2Cl_2 during $SOCl_2$ exposure on MoO_3 after a previous O_3/O_2 exposure. The parent $MoO_2Cl_2^+$ ion intensities are observed in a cluster of peaks around m/z 200. All of the main ion intensities are explained by the natural isotopic abundances of Mo and Cl in MoO_2Cl_2.

4:45pm **ALE-MoA-14 Non-Halogen Plasma for Selective Removal of Titanium Compounds Applied in Advanced Atomic Layer Etching*, Thi-Thuy-Nga Nguyen,*** Nagoya University, Japan*; K. Shinoda,* Hitachi, Ltd., Japan*; S. Hsiao,* Nagoya University, Japan*; H. Hamamura,* Hitachi, Ltd., Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective removal of metal gate materials such as TiC, TiAlC, TiN, or TiAl is required in the fabrication of next generation field effect transistor (FET) of logic semiconductor devices. In our development of advanced etching methods, we have proposed wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability). For atomic layer etching (ALE) processes, surface modification reduces surface energy of sample surface in the first step, and the modified layer is removed in the next step.

Surface modification of metal carbide TiAlC using floating wire-assisted non-halogen vapor plasma, that can generate a high-density plasma at medium pressure, has been demonstrated in our recent study, indicating a potential of isotropic and selective etching of TiAlC by using chemistries containing NH, H, and OH. In this study, the N-H-O containing plasmas can selectively remove TiAlC over TiN. Film thickness change of titanium compounds was measured by an *in situ* ellipsometer, and surface chemical bonding during the processing was analyzed by an *in situ* attenuated total reflectance-Fourier transform infrared spectrometer. Optical emission spectra of NH and OH molecular lines from plasmas were detected by a high-resolution optical emission spectrometer. The sample surface was analyzed before and after the plasma treatment by X-ray photoelectron spectroscopy.

By controlling the surface reactions, selective removal of TiAlC over TiN can be achieved by its reaction with N-H-O plasma to form volatile products, as firstly proposed here. We emphasized that this non-halogen etching method can be applied for highly selective etching of metal carbide, nitride, or oxide.

5:00pm **ALE-MoA-15 Leveraging Surface Nitridation to Enable Plasma-Thermal Atomic Layer Etching of Ni Based Metals*, Taylor Smith,*** *J. Chang,* University of California, Los Angeles

Metals are of increasing importance in modern electronics. For example, Ni and Ni-based alloys have been used for extreme ultraviolet lithography (EUVL) absorber layers and as components in composite multiferroics for magnetoelectric devices. In this work, we present an atomic layer etching (ALE) technique to etch Ni that relies on plasma nitridation to modify the Ni surface and organic vapor exposure to remove the modified layer. Theoretical study by density functional theory has shown that ALE of metals including Ni is possible through nitridation and formic acid (FA) exposure, through the formation of dimeric $Ni_2(HCOO)_4$ and NH_3 as reaction products.[1] Since surface nitridation is not a spontaneous reaction like oxidation upon exposure to ambient air (e.g., moisture), this process can be analyzed more definitively without the convolution of native oxide formation.[2] In this work, we experimentally examined this new method using a remote nitrogen plasma and a custom vapor chamber to modify and etch nickel and nickel based alloys.

A pure nitrogen plasma in a custom planar geometry ICP reactor was used to form the nickel nitride.The thickness of the nitridized layer is controlled by modifying the power, pressure, and exposure time of the plasma and quantified by a combination of spectroscopic ellipsometry (SE) and scanning electron microscopy (SEM).To alleviate the complication in SE analysis by the fact that the optical constants of thin metal films can vary depending on deposition method and thickness, SE measurements of samples that have undergone similar numbers of ALE cycles are fit simultaneously assuming that the optical constants over a narrow thickness range are the same. This improves the thickness measurement accuracy, as corroborated by SEM analysis. FA in the solution phase and vapor phase are both examined as a means of removing the nitridized Ni layer, with X-ray photoelectron spectroscopy (XPS) showing both phases completely removing the N 1s peak that forms after plasma nitridation. The etch rate of Ni by nitridation and FA solution is 6.1 nm/cycle.For the case of a Ni ALE cycle involving plasma nitridation and FA vapor exposure at 80°C, the etch rate was about 1 nm/cycle, indicating a relatively controllable process. For the Ni_xAl_y alloy, both solution phase and vapor phase FA at 80˚C removed the nitridized surface layer. However, this led to Al surface enrichment, suggesting the ALE cycle preferentially etched Ni over Al. The selectivity to common hardmasks was also tested.

References

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2. X. Sang, E. Chen and J. P. Chang, J. Vac. Sci. Technol. A **38** (4), 042603 (2020).

5:15pm **ALE-MoA-16 Plasma Atomic Layer Etching of Ruthenium with Surface Fluorination and Ion Bombardment for Next-generation Interconnect Metal***, **Yongjae Kim**, H. Kang, M. Choi, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Cu is widely used for interconnect metal in semiconductor devices, but the resistance of Cu increases significantly as the interconnect width decreases below 10 nm due to electron scattering at grain boundary and surface. Ruthenium is one of the candidate materials to replace Cu as the interconnect metal because resistivity of Ru is lower than that of Cu when the interconnect width is less than 10 nm. [1] Reactive ion etching (RIE) is used for direct patterning of metals, but controlling atomic-level film thickness in nanopatterning processes is challenging. Atomic layer etching (ALE) is suggested as an alternative to RIE because ALE can remove layers with atomic scale precision, excellent uniformity, and low surface roughness. [2]

In this work, plasma ALE process was performed for Ru in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface fluorination with CHF_3, C_4F_8 or CF_4 plasmas and ion bombardment with Ar plasma. The CHF_3 and C_4F_8 plasmas generate fluorocarbon layer on the Ru surface and the CF_4 plasma converts the Ru surface to RuF_x. The C_4F_8 plasma produces fluorine-rich fluorocarbon layer on the Ru surface compared to the CHF_3 plasma. Etch per cycle (EPC) of Ru was investigated according to ion energy and etching time. ALE window of Ru was observed in the ion energy range of 150 ~ 200 V for CHF_3 and C_4F_8 plasmas and 100 ~ 200 V for CF_4 plasma. The EPC of Ru was determined to be 0.6 nm/cycle for CHF_3 plasma, 1.5 nm/cycle for C_4F_8 plasma, and 0.3 nm/cycle for CF_4 plasma in the ALE window region. Chemical sputtering threshold energy of Ru was determined to be 100 V for CHF_3 plasma, 50 V for C_4F_8 and CF_4 plasmas. The EPC of Ru was increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for CHF_3 plasma and at 300 seconds for C_4F_8 and CF_4 plasmas. Surface roughness and etch residues of Ru were compared with RIE and ALE.

References

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Keywords: Atomic layer etching, Ruthenium etching, Fluorine-contained plasma, Surface roughness, Etch residues

5:30pm **ALE-MoA-17 Comparison of Ruthenium ALE based on ICP and Ion Beam***, D. Kim, H. Kwon, Y. Jang, H. Gil, D. Kim, G. Kim, **Geun Young Yeom**,* Sungkyunkwan University, Republic of Korea

In this study, using etching tools based on both ICP system and ICP-ion beam system, Ru ALEs have been carried out and their etch characteristics were compared. For Ru ALE based on ICP system, RuO_x was formed on the surface using direct O_2 plasma in the ICP system and then RuO_x was removed from the surface using Ar plasma by biasing the substrate. For Ru ALE based on ICP-ion beam system, and where, plasma source and the substrate were separated by grids on the ICP-ion beam source, only O radicals were supplied to the Ru surface using remote plasma to form RuO_x, and then RuO_x was removed using an Ar^+ ion beam. Using both Ru ALE techniques, surface oxidation characteristics according to direct plasma and remote plasma were compared, and desorption methods for realizing ideal atomic layer etching were investigated. In addition, physical and chemical changes occurring on the Ru surface during adsorption and desorption steps were evaluated, and the etching mechanisms were compared.

Author Index

Bold page numbers indicate presenter