

## Atomic Layer Etching

### Room Baekeland - Session ALE1-MoA

#### ALE of Metals and Alloys

**Moderators:** Heeyeop Chae, Sungkyunkwan University (SKKU), Alfredo Mameli, TNO/Holst Center

1:30pm **ALE1-MoA-1 Mechanistic Insights into Thermal Dry Atomic Layer Etching of Metals and Alloys, Andrew Teplyakov**, University of Delaware  
**INVITED**

The mechanisms of thermally induced reactions of atomic layer deposition (ALD) and atomic layer etching (ALE) can be in sometimes viewed as proceeding in opposite directions. However, for atomic layer processing of metals, that would mean that the best designed and most efficient reaction pathways leading to metal deposition would produce insurmountable energy barriers for a reverse process to occur spontaneously. If ligand detachment, exchange, and decomposition could be desirable for ALD, the etching of the same metals would require careful consideration of the etching mechanisms at the atomic and molecular level. Given that the mechanisms of ALE can be very complex, the key concepts and approaches will be described here for thermal dry etching processing and for distinguishing thermodynamic and kinetic regimes of etching. The mechanistic investigation of thermal dry etching of cobalt, iron, and CoFeB alloy will be the primary target of this work. The effects of surface oxidation and chlorination will be explored as a means to kinetically control the process, and preferential etching of one of the components of the alloy will be considered. Finally, a number of potential effects of the mechanisms of dry etching on the morphology of the surfaces produced and, specifically, on the "smoothing" effect of dry etching will be discussed.

2:00pm **ALE1-MoA-3 Thermal Atomic Layer Etching of Nickel 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 - 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 ALE is developed by first changing the Ni oxidation state by chlorination using SO<sub>2</sub>Cl<sub>2</sub>. Subsequently, the Ni is etched by the binding of P(CH<sub>3</sub>)<sub>3</sub> (PMe<sub>3</sub>) ligands that can volatilize the nickel 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, Ni has 10 d-electrons and Ni complexes typically have NiX<sub>2</sub>L<sub>3</sub> or NiX<sub>2</sub>L<sub>2</sub> configurations to obey the "18 electron rule" or "16 electron rule". The goal for Ni ALE is then to create volatile nickel compounds that are either NiX<sub>2</sub>L<sub>3</sub> or NiX<sub>2</sub>L<sub>2</sub> formed by sequential SO<sub>2</sub>Cl<sub>2</sub> and PMe<sub>3</sub> surface reactions. The proposed surface chemistry for Ni ALE (Figure 1) assumes SO<sub>2</sub>Cl<sub>2</sub> exposure leads to NiCl<sub>2</sub> on the Ni substrate. Then the NiCl<sub>2</sub> is volatilized by binding with PMe<sub>3</sub> to form either NiCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> or NiCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>.

To demonstrate this approach, Ni ALE was studied using in situ quartz crystal microbalance (QCM) and ex situ X-ray reflectivity (XRR) measurements. The in situ QCM measurements at 200 °C revealed pronounced mass increases during chlorination with SO<sub>2</sub>Cl<sub>2</sub> exposures and mass decreases during volatilization with PMe<sub>3</sub> exposures. The ex situ XRR measurements monitored the linear reduction in Ni thickness versus number of Ni ALE cycles. Ni etch rates were temperature dependent and varied from 0.39 Å/cycle at 125 °C to 2.16 Å/cycle at 200 °C (Figure 2). The nickel substrate was also examined versus number of Ni ALE cycles using scanning electron microscopy (SEM). The SEM images were homogeneous during the initial etching. However, there was evidence for surface pitting after 60-100 Ni ALE cycles at 150 °C.

2:30pm **ALE1-MoA-5 Thermal-Plasma ALE on Selected Metals for EUV and Integration Processes, Xia (Gary) Sang, E Chen, J Chang**, University of California Los Angeles

Nanometer-level metal patterning is receiving increasing amount of attention as they find application in back-end of line (BOEL) integration and as mask materials in Extreme Ultra-Violet (EUV) lithography. These metals are often etch-resistant, thus an effective chemical etching process needs

to be developed with atomic-scale level of controllability, including uniformity and selectivity. In this talk, atomic layer etching (ALE) of Cu and Ni, for their intended application in BOEL and EUV are presented.

The unique aspect of this ALE process is the combined effect of directional chemical ions and isotropic reactive neutrals. Specifically, ALE of Ni and Cu thin film is realized using sequential surface modification by directional plasma oxidation and removal of the modified surface layer by isotropic gas phase formic acid exposure. Both blanket and patterned samples were studied using this reaction scheme. A etch rate of 3 to 5 nm/cycle is determined from the blanket samples, and final features with sidewall angle of 87 is obtained on patterned samples. The effectiveness of the approach is chemically confirmed by the measuring the increase and decrease of the signals of metal oxide peaks using XPS. Etched thickness and final feature geometry are determined by SEM and TEM.

With proper chemistries and experimental conditions, this thermal-plasma ALE is capable of delivering highly selective and anisotropic patterning of metals by creating the chemical contrast and its directionality by a reactive ion while removing the modified layer entirely with an isotropic chemical processes. Applications such as next-generation logic and spintronic memory devices could benefit greatly from this patterning approach. It is expected that the approach is generalizable to a broader selection of metals.

2:45pm **ALE1-MoA-6 Thermal-Cyclic Atomic Layer Etching of Cobalt via Organometallic Complex, Sumiko Fujisaki, Y Yamaguchi, H Kobayashi, K Shinoda, M Yamada, H Hamamura**, Hitachi, Japan; M Izawa, Hitachi High-Technologies, Japan  
**INVITED**

Isotropic atomic-layer etching (ALE), which produces atomically precise removal, will have an important role in semiconductor manufacturing. This is because highly selective ALE has become necessary to deal with processing of new materials in miniaturized 3D devices. In the past several years, isotropic ALE of various materials has been reported which includes thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concerning the variety of materials to be etched, isotropic ALE of cobalt must be developed. Thermal ALE of cobalt has been reported by using treatment with formic acid and ligands to produce volatile cobalt complexes [2]. Also, the authors have successfully demonstrated isotropic ALE of cobalt film with smooth etched surfaces, which is important issue in the development of ALE of cobalt [3].

Experimental apparatus used in this study is 300-mm ALE tool equipped with inductively-coupled plasma source and infrared (IR) lamps. One cycle of this thermal-cyclic ALE process is roughly divided into two steps: oxidation and organometallization. In the first step, surface of cobalt film is oxidized by oxygen plasma at low temperature. In the second step, the cobalt oxide is converted into organo-cobalt complex by diketone at high temperature. The organo-cobalt complex then desorbs from the film surface because of its higher volatility. Processing condition is optimized so that the cobalt oxide layer formed in the first step is completely removed in the second step. Thus, etched amount can be controlled by oxidation thickness of cobalt and number of cyclic repetitions. Temperature cycle is important to obtain smooth etched surface. Our ALE tool produces short processing time because it is equipped with IR lamps for rapid heating. The mechanism of the surface reaction of the cobalt ALE was examined by x-ray photoelectron spectroscopy (XPS). Several oxygen 1s peaks were detected in the range from 525 to 535 eV after the first oxidation step. A peak at 530 eV decreased after the sample was exposed to diketone. This result implies that the peak at 530 eV, which is ascribed to a certain oxidation state of cobalt, dominantly contributes to formation and desorption of diketone-cobalt complex.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. **50**, 194001 (2017).

[2] C. Winter, AVS 65<sup>th</sup>, PS+EM+TF-ThM5 (2018).

[3] S. Fujisaki et al., ALE Workshop, ALE1-TuM8 (2019).

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