Atomic Layer Etching
Room Hall 3F - Session ALE2+AM-TuA
A.I. for ALD and ALE, and Wet-Chemical ALE

Moderators: Eric Liu, Tokyo Electron America, USA, **Kazunori Shinoda**, Hitachi High-Tech Corporation

4:00pm **ALE2+AM-TuA-11 Application of Machine Learning to Atomic-Scale Process Development*, Satoshi Hamaguchi,*** Osaka University, Japan **INVITED**

For the development of new atomic-scale processing such as atomic layer etching (ALE) and atomic-layer deposition (ALD), efficient selection of precursor gases and other process conditions is desired among a large number of possible combinations of them. Artificial intelligence (AI) and machine learning (ML) techniques are expected to facilitate this selection. In this presentation, after briefly reviewing recent developments in data-driven plasma science [1] for process development and control in general,we discuss a method to predict the sputtering yields/etch rates of materials by ion impact based on experimental and simulation data of sputtering yields/etch rates. In such predictions, the sputtering yield typically depends on a relatively small number of physical parameters that characterize the surface material and incident ions (such as the masses of the surface material atoms and incident ions). However, the availability of large sputtering yield data is crucial for accurate prediction. Because experimental data for specific material and ion combinations may not be available, physics-based numerical simulations can be used to augment these data. For example, classical molecular dynamics (MD) simulations can be used to provide sputtering yield data but interatomic force-field models for “unfamiliar” materials are often of questionable accuracy. A method to develop ML-based interatomic force-field models is presented with an example of Si etching, and the challenges of such methods for general materials are discussed.

[1]R. Anirudh, et al., “2022 Review of Data-Driven Plasma Science” IEEE Trans. Plasma Sci. 51(7) 1750-1838 (2023).

4:30pm **ALE2+AM-TuA-13 Surrogate Models for One-Shot ALD and ALE Process Transfer Across Reactors and High Aspect Ratio Substrates*, Angel Yanguas-Gil,*** *J. Elam,* Argonne National Laboratory

Being able to predict the behavior of ALD or ALE processes when transferred from a lab setting to manufacturing would help accelerate the adoption of ALD and ALE in a wide range of applications, from energy materials to microelectronics. Current approaches require extensive tool time and characterization or, when assisted by simulations, accurate models carefully tuned to each specific process. In addition to reducing the risk and cost of adopting new processes, being able to predict the behavior of a specific precursor across reactors and types of substrates can also be used to discriminate processes that struggle to perform well under more challenging conditions present in manufacturing. A key challenge is our lack of information about many ALD and ALE processes. This includes not only the surface kinetics, but in many cases the precursor pressure in the reactor or upstream precursor consumption. It is therefore key to understand how can we compensate for this lack of information with more readily available experimental data.

In this work, we tackle this problem from a machine learning perspective. In particular, we have focused on using surrogate models as tools to help us understand the following two questions: 1) how can we predict process performance across reactors and substrates?; 2) what are the key experimental observables that we need in order to make such connection? Building on our prior work on artificial neural networks for ALD process optimization,[1] we constructed surrogate models trying to connect experimental data under lab conditions with key process metrics relevant for manufacturing. These include predicting throughput, precursor utilization, process variability across large area substrates, or expected conformality. These models are built using datasets from simulations that have been shown to agree well with experimental data for a few known processes, such as Al_2O_3 growth from trimethylaluminum and water.[2] Our results show that a careful experimental design involving the characterization of film thickness at predefined reactor conditions under undersaturated conditions is often enough to compensate for the lack of knowledge of a specific process. The downside is that the surrogate models are dependent on the specific reactor geometry. However, within a given reactor, surrogate models show predictive behavior across a wide range of surface kinetics and precursor pressures as long as the process kinetics is represented in the training set.

[1] A. Yanguas-Gil and J. W. Elam, *J. Vac. Sci. Technol. A* 40, 062408 (2022)

[2] A. Yanguas-Gil, J. A. Libera and J. W. Elam, *J. Vac. Sci. Technol. A* 39, 062404 (2021)

4:45pm **ALE2+AM-TuA-14 Ligand-Assisted Surface Layer Formation in Wet Atomic Layer Etching of Molybdenum*, Tulashi Dahal,*** *K. Abel,* Tokyo Electron America Inc.*; N. Levtchin,* TEL Manufacturing and Engineering of America, Inc.*; T. Hurd,* Tokyo Electron America Inc.,*; A. Rotondaro,* Tokyo Electron America Inc.

There are many applications for molybdenum in the semiconductor industry including metallization in logic BEOL and 3-D NAND. These applications often require partial etch back where the post-etch morphology is critical to device performance. Wet atomic layer etching (ALE) offers materials removal with Angstrom-level precision following two sequential, self-limiting, wet processing steps. In the first step, a Mo surface is exposed to an oxidizing solution that forms a self-limiting oxidation layer. In the second step, this layer is selectively dissolved in a second solution. Formation of a self-limiting Mo oxidation layer is challenging due to the solubility of molybdenum oxides in aqueous solution, which leads to continuous Mo etch and rougher post-etch morphology. Solubilization of Mo oxides can be delayed in a non-aqueous oxidizing solution. Mo surface oxidation in non-aqueous solution is, however, not self-limiting (Fig. 1). The post-etch morphology of Mo in cyclic etch experiment using non-aqueous oxidizing solution is rougher compared to the starting coupon owing to preferential grain boundary etching. Here we present our results on improving the self-limiting nature of Mo oxidation layer by adding a ligand to the oxidizing solution. Aqueous oxidation of Mo leads to a continuous etch, non-aqueous oxidation leads to a delayed etch, but adding a ligand to the oxidation solution leads to the formation of a stable passivation layer (Fig. 1). Cyclic etch experiments were carried out to estimate the Mo etch rate by exposing the Mo coupon in non-aqueous solution with and without a ligand. The drop in Mo ER from ~0.10 nm/cycle to ~0.07 nm/cycle after adding millimolar amount of ligand in the oxidizing solution indicates the changes in surface chemistry with ligand (Fig. 2). The dissolution of modified layer can be significantly increased via enhanced dissolution kinetics at an elevated temperature nearly doubling the Mo etch rate (~0.12 nm/cycle). Mo ER (~0.12 nm/cycle) is constant from 5 mM to 100 mM of ligand and drops to ~0.08 nm/cycle for higher ligand concentration remaining constant thereafter. The drop in Mo etch rate with higher ligand concentration may be attributed to the piling up of surface products that are less soluble in the dissolution chemistry B. The measured RMS roughness and the SEM images (Fig. 3 and inset) show that addition of a ligand decreases the post-etch surface roughness to the level of the unetched reference coupon. We attribute these differences in etch rate and post-etch morphology to improvements in the conformality and self-limiting nature of the surface oxidation layer with the addition of a ligand.

5:00pm **ALE2+AM-TuA-15 Wet Atomic Layer Etching of Ruthenium*, Kate Abel,*** Tokyo Electron America, Inc.

We have developed a new process chemistry for atomic layer etching (ALE) of ruthenium (Ru) using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through selective dissolution of a self-limiting passivation layer rather than volatilization. In wet ALE, a self-limiting surface layer is chemically formed upon exposure to the first etching solution. The surface layer must be insoluble in this solution, but readily soluble in the second etching solution in order to complete the ALE cycle. The dissolution of the surface layer in the second solution mayoccur either through intrinsic solubility of the modified layer or through a selective reactive dissolution process. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is therefore required for material removal. A diagram of this process is shown in Figure 1.

Forming a self-limiting layer on Ru that is capable of being selectively solubilized in a second solution is challenging. The common oxides, RuO_2 and RuO_4, are unsuitable – RuO_2 requires harsh, non-selective chemicals to be removed and the low melting point, volatility, and high solubility of RuO_4 prevent the formation of a stable passivation layer. Many non-oxide Ru compounds are known. Synthesis from the metallic state, however, generally requires oxidation to less stable intermediate oxidation states.

In this talk, we show that self-limiting passivation of the Ru surface can be accomplished by controlling both the oxidation potential and co-reactants present in solution. We pair an oxidizer with a variety of co-reactants in solution to show that the chemistry at the Ru surface can be changed from a continuous dissolution process to the formation of a self-limiting surface layer by changing the identity of the co-reactant. In the self-limiting case, completion of the wet ALE cycle can be accomplished through reactive dissolution of the Ru surface layer in a second etching solution. We present quartz crystal microbalance data to show how the oxidation conditions, co-reactant identity, and dissolution conditions influence the behavior of the Ru surface in this cyclic etch process.

5:15pm **ALE2+AM-TuA-16 Combined Dry-Wet ALE for Tungsten: A Surface Characterization Study***, **Cinzia Chan,*** KULeuven, Imec, Italy*; J. de Marneffe,* IMEC, Belgium*; C. Gort,* TU Darmstadt, Germany*; J. Serron, M. Agati,* IMEC, Belgium*; J. Hofmann,* TU Darmstadt, Germany*; S. De Gendt,* KULeuven, Imec, Belgium*; D. van Dorp,* IMEC, Belgium

The continuous device scaling towards atomic-scale dimensions is facing challenges due to increasing complexity at both architecture and structure level. At these scales, the requirements for etching processes are limited to angstrom level. Therefore, atomic layer etching (ALE) and cleaning (ALC) are currently extensively studied as they utilize self-limiting reactions to etch surfaces with high control.

Tungsten is a material of high interest as it is currently being explored for MRAM and spintronic applications[1,2]. The reported ALE processes are halogen-based plasma[3,4] and often require high temperatures (>200˚C) to form volatile byproducts[5,6]. However, limitations on the thermal budget and the use of plasma processes may be incompatible or detrimental to the exposed materials in the device stack. Therefore, we propose a combined dry-wet ALE approach that consists of a self-limiting oxidation step (dry) combined with a selective oxide removal step in acidic solution. The advantage of a selective wet etch is that it does not induce any physical or structural damage (e.g. amorphization) as compared to a full dry approach.

The proposed dry-wet ALE method was investigated on W blanket layers and patterned structures. Surface oxidation was performed through an $O\text{--}_2$ plasma treatment at 60˚C, followed by oxide product removal in dilute HCl solution at RT. Inductively coupled plasma mass spectrometry (ICP-MS) was used to study oxide etching kinetics and selectivity by quantification of the etched surface density of W in time. During the first minutes a rapid removal of W oxide was observed followed by a gradual lowering of the etched surface density towards a constant level that corresponds to the background etch rate of the metal. An oxide/metal etch selectivity of ~100 was found. Selectivity could be further improved by lowering the dissolved O_2 concentration in the etchant. While ICP-MS quantification and TEM inspection revealed that the bulk of the oxide is removed within 20 minutes, post-operando XPS measurements confirmed that a remaining interfacial (sub)oxide monolayer was only removed after 60 minutes of immersion in the acid. Conductive AFM measurements agreed with these observations. The etch per cycle was 0.8nm/cycle while the surface morphology was maintained.

[1] K. Kumar *et al.*, *Phys. Rev. Appl.*, 10, 1, 2021

[2] M. Costa *et al.*, *J. Phys. Condens. Matter*, 30, 305802, 2018

[3] D. S. Kim *et al.*, *Plasma Process. Polym.*, 16, 9, 2019

[4] K. Shinoda *et al., Proc. of SPIE,* 10589, 1, 2024

[5] N. R. Johnson *et al.*, *ACS Appl. Mater. Interfaces*, 9, 34435, 2017

[6] W. Xie *et al.*, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, 38, 022605, 2020

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