## Plasma Science and Technology Division
## Room A107-109 - Session PS2+MS-WeA

## Plasma-Surface Modeling

**Moderators: Emilie Despiau-Pujo**, Univ. Grenoble Alpes, CNRS, LTM, **Jun-Chieh Wang**, Applied Materials

2:20pm **PS2+MS-WeA-1 Modeling and Simulation of Plasma-Surface Interactions in Nanofabrication***, **David Graves**,* Princeton University **INVITED**

Plasma-enhanced atomic layer deposition (ALD) and etching (ALE) in principle offer an unprecedented opportunity to control surface composition and structure. By modulating process time, frequency, energy, and chemistry, it is possible to vastly increase the range of conditions and surface modification effects at surfaces. ALE/ALD can simplify the process by separating, for example, a chemical surface modification step from addition of energy through rare gas ion bombardment. It might be possible to design novel etch and/or deposition precursor molecules to take advantage of ALE/ALD modulation-oriented approaches. However, process modulation introduces the complexity of having the surface state change in time during the exposure. To understand and control these processes, an atomic scale plasma-surface interaction simulation is essential. In this talk, I briefly review the use of molecular dynamics (MD) simulations in plasma-surface interactions and how they have been used to help understand conventional plasma etching and deposition. I then use our recent studies of PEALE to highlight both successes and limitations of the current state of the art when used for modulated atomic layer processes. The key issues of interatomic force fields for many new chemistries and materials; using MD to simulate an intrinsically multi-timescale process; and the need to couple well-diagnosed experiments with atomistic simulations are emphasized.

3:00pm **PS2+MS-WeA-3 Mechanisms of Phosphorus Halides Gas Boosting Cryogenic Dry Process Etch Rate: A Quantum Chemistry Investigation***, **Yu-Hao Tsai**, D. Zhang,* TEL Technology Center, America, LLC*; T. Orui, T. Yokoyama, R. Suda,* Tokyo Electron Miyagi Limited, Japan*; T. Hisamatsu,* TEL Technology Center, America, LLC*; Y. Kihara,* Tokyo Electron Miyagi Limited, Japan*; P. Biolsi,* TEL Technology Center, America, LLC

3D-NAND fabrication requires ultrafast etch rate (E/R) of the dielectric material stacks to deliver the high-aspect-ratio contact (HARC) etch with an economical fashion. In a sperate report submitted about the cryogenic dry etch process development, we introduce the results of the drastically higher E/R of Ox/SiN (ONON) than the room temperature ones. We also reveal the catalytic etching reaction which enables the fast-etch process. We then identify the E/R booster gases: phosphorus halide, which brings the E/R to a higher level. To advance the booster-process development, a fundamental understanding of how the performance enhancing gases work is unavoidably crucial. This paper focuses on the mechanisms of phosphorus halides booster making the ONON E/R faster than the non-boosted cryogenic etch processes. Using the density functional theory (DFT), we identify the major chemical reactions behind the E/R enhancement. Based on the findings, we highlight the major properties required for the booster gases to function. The experimental results verify the mechanisms built upon the DFT study. In addition, we discuss the impact from the halogen atoms of the molecules on the etch performance. The paper does not only provide the insight toward an even higher E/R but also shed a light on the synergy of combing the experiments and atomistic modeling for the advanced node manufacturing technology developments.

3:20pm **PS2+MS-WeA-4 Molecular Dynamics Simulations of Diamond Surface Processing via Low-Energy Hydrogen and Argon Ion Bombardment***, **Jack Draney**,* Princeton University*; J. Vella,* Princeton University Plasma Physics Lab*; A. Panagiotopoulos, D. Graves,* Princeton University

Nitrogen-vacancy (NV) centers in diamond are promising for multiple applications in quantum information processing and sensing [1,2]. NV centers can locally detect and measure physical quantities such as magnetic and electric fields. However, these devices are currently limited by surface defects that compromise charge stability and spin coherence [1,2]. In this work, we explore plasma-assisted atomic layer etching of diamond using classical molecular dynamics (MD) simulations. We performed MD simulations of low-energy hydrogen (<50 eV) and argon (<200 eV) ion bombardment of diamond surfaces. Argon ion bombardment can be used to locally smooth initially rough diamond surfaces via the formation of an amorphous C layer, the thickness of which increases with argon ion energy. Subsequent exposure with hydrogen ions (or fast neutrals) will selectively etch this amorphous C layer, leaving the underlying diamond layer intact if the H energy is maintained between ~2–5 eV. The simulations suggest that combining $Ar^+$ smoothing with selective H removal of amorphous C could be an effective strategy for diamond surface engineering, leading to more reliable and sensitive NV center devices.

[1] Sangtawesin, S., Dwyer, B. L., Srinivasan, S., Allred, J. J., Rodgers, L. V., De Greve, K., ... & De Leon, N. P. (2019). Origins of diamond surface noise probed by correlating single-spin measurements with surface spectroscopy. *Physical Review X*, *9*(3), 031052.

[2] Stacey, A., Dontschuk, N., Chou, J. P., Broadway, D. A., Schenk, A. K., Sear, M. J., ... & Hollenberg, L. C. (2019). Evidence for primal sp2 defects at the diamond surface: candidates for electron trapping and noise sources. *Advanced Materials Interfaces*, *6*(3), 1801449.

4:20pm **PS2+MS-WeA-7 Yesterday, Today, and Tomorrow for High-Aspect-Ratio Contact Etching: Unraveling the Mysteries of Plasma-Surface Interactions with Modeling and Simulations***, **Du Zhang**, Y. Tsai,* TEL Technology Center, America, LLC*; M. Iwata, M. Yokoi, K. Tanaka,* Tokyo Electron Miyagi Limited, Japan*; T. Hisamatsu,* TEL Technology Center, America, LLC*; Y. Kihara,* Tokyo Electron Miyagi Limited, Japan*; P. Biolsi,* TEL Technology Center, America, LLC **INVITED**

The ever-growing demand for big data storage and processing has driven advancements in both the design and process technologies of advanced memory devices. In particular, the fabrication of high-aspect-ratio contacts (HARC) is a key process step. Etch throughput and profile control are crucial for reducing manufacturing cost and ensuring device performance. To meet these challenges, multiscale mechanistic understandings are essential for driving process and design optimization.

In this paper, we will discuss the fundamental etch mechanisms of plasma-surface interactions for HARC etching assisted by atomistic / plasma / profile modeling. We will review the underlying surface reaction mechanisms of the conventional fluorocarbon gas chemistry. We will also discuss the typical process challenges with etch rate and profile control, as well as various possible mitigation methods. Moreover, we will introduce how hydrogen admixture into the fluorocarbon chemistry can alter the behavior of dielectric etch rate and surface chemistry in a way that breaks conventional wisdom, especially at lower wafer temperatures. By unraveling and utilizing these underlying mechanisms derived from multi-scale simulations, we have been able to design new processes to achieve enhanced performance.

5:00pm **PS2+MS-WeA-9 Optimization of Model Parameters in Simulations of High Aspect Ratio Plasma Etching***, **Florian Krüger**,* University of Michigan, Ann Arbor*; D. Zhang, M. Park, A. Metz,* TEL Technology Center, America, LLC, USA*; M. Kushner,* University of Michigan, Ann Arbor

Computational investigations of feature evolution during plasma etching of micro- and nano-electronics devices are highly dependent on a robust reaction mechanism and precise knowledge of reaction probabilities and coefficients to accurately represent the physical behavior of these processes. The increased complexity of the structures and use of novel gas compositions coupled with the necessarily reduced reaction set used by numerical investigations of feature evolution makes it difficult to choose these critical parameters from first principles. This problem is exacerbated by the fact that many of the physical and chemical processes occurring during plasma etching are based on different fundamental principles - i.e., physical sputtering, chemical sputtering, chemisorption, physisorption, spontaneous etching – that have different functional forms.

The aim of this work was to accelerate the development of reaction mechanisms for feature profile evolution during plasma etching.This is accomplished by selecting a subset of reaction rates and angular dependencies and matching the predictions of feature profiles to experimental data using autonomous optimization methods. To that end a series of etches of high aspect ratio (HAR) $SiO_2$ features using a $C_4F_6$ / $C_4F_8$ / Ar /$O_2$ plasma was performed and relevant quantities such as etch depth, etch rate, aspect ratio as well as critical widths at several depths were determined using scanning electron microscopy.

The same process was reproduced using gas phase and profile scale simulation tools, HEPM (Hybrid Plasma Equipment Model) and MCFPM (Monte Carlo Feature Profile Model), respectively. Some of the input parameters used by the MCFPM were coupled to a multi variate 2-step optimizer that adjusted relevant input parameters in to achieve the best match between simulation and experiments.Thus, the profile etch simulation effectively acts as an objective function on which the optimization is based. Due to the specific nature of the data and objective function with respect to spatial discretization, the 2-step approach – a combination of gradient descent and Nelder-Mead optimization - proved most effective.

The outcome and development this optimization process will be discussed.The resulting reaction mechanism was used to simulate features using similar but quantitatively different processing conditions to demonstrate how broadly the mechanism can be applied.

---

* Work supported by Tokyo Electron, Samsung Electronics and the National Science Foundation.

5:20pm **PS2+MS-WeA-10 Prediction of Surface Morphology and Composition Evolution during Atomic Layer Deposition via Combined Ab-Initio and Monte Carlo Approach***, **Ting-Ya Wang**, G. Hwang,* University of Texas at Austin

Atomic layer deposition (ALD) has been proposed as a method for achieving greater precision and control over film thickness, conformality, and impurity levels as compared to traditional chemical vapor deposition. It uses alternating cycles of two half-cycle reactions to achieve sequential and self-limiting deposition. However, finding the optimal conditions for the desired film properties and surface states for a certain material has largely relied on a trial-and-error approach. To expedite the search process, understanding the underlying mechanisms that influence surface chemistry and structure is crucial. However, currently available experimental methods may be limited in their ability to non-invasively observe surfaces at the atomic level or hindered by overlapping signals.

Theoretical methods have their own set of limitations. First-principles calculations, such as density functional theory (DFT), can be used to study the electronic structure of atoms and have been applied extensively to study surface reaction pathways. However, they are generally limited to a few hundred atoms and do not consider temperature and pressure effects. Ab-initio molecular dynamics (AIMD) simulations allow for studying dynamic processes, but they are similarly limited by both length and time scales. Monte Carlo (MC) simulations provide a way to study the thermodynamic properties of larger systems, and kinetic MC (KMC) allows for real-time simulation of system evolution. However, without a description of potential for each atom, both MC methods rely on predetermined lists of allowed events, which limit their accuracy and applicability.

Combining MC with DFT can potentially enhance the accuracy and applicability of simulations. However, in order to make these methods more reliable in describing various systems and include unknown reaction mechanisms, streamlining the integration of these two methods and the auto-generation of required information for MC simulations is important. In our work, we have applied this approach to investigate the evolution of surface structure and film morphology during plasma-enhanced ALD. Film morphology is a critical factor affecting film properties such as refractive index and wet etching rate, while surface structure determines the surface chemistry and thus affects deposition kinetics. We have examined the effects of plasma and different types of precursors on ALD processes and film properties, as well as the impact of process conditions, such as temperature and pressure.

5:40pm **PS2+MS-WeA-11 Modeling Reaction and Diffusion at a Plasma-Liquid Interface***, **Sean Peyres**,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; N. Abuyazid, R. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas can promote reactions at a liquid surface for various applications including nanoparticle synthesis, water purification, treatment of skin wounds, and chemical production. At the core of these processes, plasma-produced species, such as electrons and hydroxyl radicals, cross the gas-liquid boundary and rapidly react with solution-phase species, including the solvent, within a few nanometers to micrometers distance of the interface. A key consequence of the highly localized reactions is that the reaction rates are limited by mass transport of the solution species from the bulk liquid to the plasma-liquid interface. Previous experimental studies have observed such mass transport limitations, but a fundamental description of the mass transport has yet to be developed.

Here, we present a simple reaction-diffusion model for the reaction of plasma-produced species at a gas-liquid interface. The model consists of a set of nonlinear differential equations describing the reaction and diffusion of a single plasma species (referred to as a radical) and a single solution-phase species (referred to as a scavenger). The plasma-produced radical reacts both with the scavenger and itself in the solvent via recombination. To solve the equations analytically, simplifying assumptions were necessary. First, quasi-steady state was assumed, where the radical and scavenger concentrations quickly obtain a profile that can be solved for a given time. Then, various assumptions were made to solve the equations under limiting cases. Examples include negligible radical-scavenger reaction, uniform scavenger concentration, and fast reaction with the scavenger (compared to radical recombination). These results could be summarized by using dimensionless numbers that relate the competition between the radical-scavenger and radical recombination reactions along with the transport freedom of the scavenger.

Furthermore, we solved the full set of equations numerically and compared with the analytical solutions for the limiting cases. Finally, by adding a boundary condition for the diffusive layer, the bulk scavenger concentration could be calculated as a function of time and compared with previous experimental reports. We show that the model can be used to quantitatively predict and explain mass transport effects on reaction yields and selectivity.

6:00pm **PS2+MS-WeA-12 Integrated Modeling of Diamond Growth and the Surface Composition in $CH_4/H_2$ Plasma***, Y. Barsukov,* Princeton University Plasma Physics Lab*; A. Khrabry,* Princeton University*; **Igor Kaganovich,*** Princeton University Plasma Physics Lab

Microwave plasma generated in a mixture of CH4 highly diluted in H2 is typically used to grow diamonds. According to the broadly accepted mechanism, most of the surface of the growing diamond is unreactive because it is covered by hydrogen atoms. At a small fraction of the surface, hydrogen is removed by the so-called hydrogen-atom abstraction mechanism resulting in the formation of reactive sites (surface activation). Radical species produced in the CH4/H2 plasma are adsorbed on the reactive surface sites, changing the surface composition and promoting the diamond film growth. Atomic H radicals play a key role in the surface activation, allowing for the CH3 radicals to be adsorbed on the reactive sites which leads to the growth of diamond. Nevertheless, the main by-product of CH4 decomposition in the plasma is C2H2, but its role in the growth process is still debated. A complex kinetic model which links fluxes of gaseous reactants from the plasma to the surface composition is needed to identify the role of each reactant.

To consider complex plasma-surface chemistry we performed a 0D kinetic modeling, where 83 surface reactions between CH4, CH3, H, H2 and C2H2 gaseous species are considered. The rates of all 83 reactions were calculated under the same approach, namely, we used WB97XD DFT functional and transition state theory. The DFT functional was validated for gaseous reactions, for which rate constants were measured. The following processes were considered in the model: 1) surface activation/passivation by H, H2, CH3 and CH4, 2) adsorption/desorption of CH3 and C2H2 on the reactive surface sites, 3) hydrogen abstraction from the adsorbates, 4) incorporation of C atom from the adsorbate into the diamond network (sp3 phase), and 5) formation of sp2 phase from C2H2 adsorbate.

The model reproduces the experimental observation that the rate of diamond growth strongly depends on the substrate temperature and has a peak near 1200 K. Detailed analysis of the surface composition shows that the growth is suppressed at low temperature due to formation of sp2 phase. (The mechanism of sp2 phase formation is similar to the mechanism of soot growth). At temperatures higher than 1200 K, the growth is suppressed due to reverse reactions leading to separation of C atoms from the diamond network into the adsorbed state and their subsequent desorption. Thus, our 0D kinetic model allows to link fluxes of plasma reagents with the surface composition and growth rate. The model will be expanded with reactions leading to doping of diamond, which are critical for the synthesis of sensors and cubits.

# Author Index

## Bold page numbers indicate presenter