Plasma Science and Technology
Room 201 ABCD W - Session PS3-WeA

ICP Modelling

Moderators: Thorsten Lill, Lam Research Corporation, **Shahid Rauf**, Applied Materials, USA

4:15pm **PS3-WeA-9 Quantum Chemistry and Integrated Modeling for Understanding the Mechanisms of Selective and Cryogenic Atomic-Scale Etching**, ***Yuri Barsukov***, *Mingmei Wang, Qing Xu, Thorsten Lill,* Lam Research Corporation **INVITED**

Plasma etching for high aspect ratio vertical trenching in 3D-structured silicon-based devises is one of the most challenging steps in advanced semiconductor manufacturing. This process requires precise control of both ion and neutral fluxes to facilitate etching at the trench bottom while ensuring sidewall passivation to prevent lateral etching and feature distortion. As the range of chemical reactants used in industry continuous to expand, a deeper understanding of plasma-surface interactions and surface reaction mechanisms becomes increasingly critical. Over the past decade, quantum chemistry has played a growing role in elucidating these mechanisms, providing valuable insights for optimizing plasma etching processes.

Quantum chemistry is widely used to investigate reaction mechanisms at the atomic level. Within the framework of transition state theory, the reactivity of various fluorine-based reactants with semiconductor materials has been calculated, revealing how etching with these reactants can be catalyzed, enhanced, and accelerated through vibrational excitation. This ab-initio approach enables the calculation of rate constants for key surface reactions and allows for the integration of surface reactions kinetics with plasma chemistry models. These kinetic models predict the dependence of etching rates and selectivity on plasma parameters. For example, the reactivity of fluorine (F) atoms and hydrogen fluoride (HF) molecules – two of the most commonly used reactants in the semiconductor industry – has been studied on silicon-based materials such as Si, SiN, and SiO_2.

Another crucial challenge in plasma-assisted etching is the efficient delivery of ions to the trench bottom. Accelerated ions lose kinetic energy through the collisions with sidewalls, leading to feature damage without effectively contributing to bottom etching. Despite their high initial energies in the keV range, the normal component of ion energy at the grazing incident is only in tens of eV. As a result, relatively weak chemical interactions between sidewall materials and incident ions play a crucial role in determining etching efficiency and feature integrity. Using ab-initio molecular dynamics, it has been demonstrated that ammonia fluoride ionic salts – the most common etching by-products that coat the sidewalls – provide more effective protection against damage and help prevent ion energy loss at lower temperatures. This discovery sheds light on the mechanisms of cryogenic plasma-assisted etching and highlights the importance of by-product formation in sustaining etching process.

4:45pm **PS3-WeA-11 Simulation of an Inductively Coupled Plasma with a Two-Dimensional Darwin Particle-in-Cell Code**, *Dmytro Sydorenko,* University of Alberta, Edmonton, AB, Canada*;* ***Igor Kaganovich****, Alexander Khrabrov,* Princeton Plasma Physics Laboratory

Electromagnetic simulation with an explicit algorithm has a severe limitation on the time step due to the large speed of light propagation resulting in the high numerical cost. Fully implicit electromagnetic algorithms do not have this limitation but are more complex to implement. Another option is the Darwin method omitting the electromagnetic wave propagation [1]. The Darwin method separates the electric field into solenoidal (electromagnetic) and irrotational (electrostatic) parts.

In this work, we propose a new Darwin scheme for simulation of low-frequency electromagnetic processes in laboratory plasmas. A two-dimensional particle-in-cell code in Cartesian geometry has been developed based on the direct implicit Darwin electromagnetic algorithm described in Ref. 1. The new code has several significant modifications compared to the original algorithm. First, the SDF is replaced by a new method based on the equation for the vorticity of the solenoidal electric field. Unlike the SDF, the linear system of equations in the vorticity method is reliably solved using a standard iterative solver. Second, the electromagnetic fields are defined on staggered grids convenient for electromagnetic simulation. Third, the contribution of collisional scattering is included in calculation of the solenoidal electric fields. Fourth, the code includes several solvers for the self-consistent magnetic field with different boundary conditions. Once one of these methods is selected for a particular simulation, the choice can be verified by checking the energy conservation.

A two-dimensional particle-in-cell code has been developed using the modified direct implicit Darwin electromagnetic algorithm described in Ref. 2. The code is a valuable tool for simulation of various electromagnetic effects, for example the inductively coupled plasmas and the electromagnetic plasma waves. The code can be used to design future plasma thrusters.

References:

[1] M. R. Gibbons and D. W. Hewett, "The Darwin Direct Implicit Particle-in Cell (DADIPIC) Method for Simulation of Low Frequency Plasma Phenomena," J. Comput. Phys. 120, 231–247 (1995).

[2] Dmytro Sydorenko, Igor D. Kaganovich, Alexander V. Khrabrov, Stephane A. Ethier, Jin Chen, Salomon Janhunen, "Improved algorithm for a two-dimensional Darwin particle-in-cell code", arXiv:2409.19559, submitted to Phys. Plasmas (2024).

5:00pm **PS3-WeA-12 Kinetic and Hybrid Modeling of a Radio Frequency Hollow Cathode Discharge and Comparison with Experiments**, ***Nakul Nuwal****, Kallol Bera, Han Luo, Xingyi Shi,* Applied Materials Inc.*; Shahid Rauf,* Applied Materials, USA*; Jan Guttmann,* Applied Materials Inc.*; Ihor Korolov, Julian Shulze,* Ruhr Universität Bochum, Germany

Radio frequency (RF) hollow cathode discharges (HCD) are used in various semiconductor manufacturing processes such as material etching and deposition. HCD cathodes have cavities, and the plasma forms inside these cavities under the right conditions. In the HCD, RF sheath heating as well as secondary electron acceleration can lead to plasma production. In this work, plasma simulation results for argon and oxygen HCDs are compared with plasma diagnostics measurements using non-invasive methods. These measurements include the emission spectra of plasma discharge using Phase Resolved Optical Emission Spectroscopy (PROES), which provides the spatio-temporal excitation rate of important species in the discharge. We use both kinetic and hybrid plasma models in this work to understand the plasma dynamics and elucidate with the experimental observations. The Particle-In-Cell with Monte Carlo Collisions (PIC-MCC) model includes evolution of charged particles and electrostatic field along with charged particle collisions with the neutral species using a Monte Carlo approach. The hybrid model only treats the electrons as particles and includes a fluid model for the other charged species. In both models, the charged species' densities are coupled with the Poisson's equation to calculate the electric potential, enabling a self-consistent plasma simulation. Plasma simulations are performed for different pressures, voltages, and feed gases (Ar & O_2). Our simulation results show good agreement with the spatio-temporal experimental measurements of metastable argon excited state at low pressures. With increase in voltage, the excited species is found to penetrate further into the hollow cathode slot. The modeling results also indicate that the secondary electron emission coefficient from surfaces significantly influences the plasma behavior.

5:15pm **PS3-WeA-13 Modeling of Remote Inductively Coupled Plasmas and Comparison to Experiments**, ***Mackenzie Meyer****, David Boris, Michael Johnson, Jeffrey Woodward, Virginia Wheeler,* US Naval Research Laboratory*; Mark Kushner,* University of Michigan*; Scott Walton,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) utilizes plasma as a source of reactive species. Using plasma enables processing at low temperature and with materials that cannot be processed using thermal atomic layer deposition. Remote inductively coupled plasmas (ICPs) are utilized in PEALD as they limit damage to the substrate. Since the plasma is spatially removed from the substrate by 10s of cm, energetic ions are limited while radicals remain plentiful at the substrate location. However, questions remain about the physics of remote ICPs downstream of the plasma source. To help unravel the physics occurring in these devices, we model a remote ICP system using the 2D Hybrid Plasma Equipment Model (HPEM). The remote ICP system is based on the Veeco Fiji G2 source. We focus on pure Ar plasmas over a range of pressures and powers. Power is coupled both inductively and capacitively to the plasma. Based on the location of the powered end of the coil, the capacitively coupled power is deposited near the exit of the ICP and into the spatial afterglow. The results of the model are benchmarked against Langmuir probe measurements at these conditions. The effect of N_2 addition to the Ar plasma is also examined and benchmarked against measurements. These results are discussed in the context of PEALD.

This work is partially supported by the Naval Research Laboratory base program.

5:30pm **PS3-WeA-14 Modeling of E-H Transition in Inductively Coupled Plasmas**, ***Ashish Sharma****, Rochan Upadhyay, Sudharshanaraj Thiruppathiraj, Dmitry Levko, Anand Karpatne, Radhika Mani,* Lam Research Corporation

E to H transition is a phenomenon observed in plasma discharges and has been known to have a significant impact on the plasma etching characteristics. In the present study, we investigate the phenomenon of E-H transition for inductively coupled plasmas. These simulations have been conducted for a 2D GEC RF Reference cell in Cl2 gas using VizGlow®. We study the transition of the plasma discharge from E-mode to H-mode and investigate the underlying physics governing the transition. We quantify the percentage of the input power absorbed in E mode and H mode and study the influence of TCP power, coil frequency and gas pressure on the power breakdown and E-H transition characteristics. Lastly, we analyze the plasma properties in E and H mode, mainly focusing on the differences in plasma densities, electron temperature and ion fluxes in these respective modes.

5:45pm **PS3-WeA-15 Exploring Radical Formation, Fragmentation, and Polymerization of Pentane and Acrylic Acid Precursors in Low Temperature Plasma**, ***Mackenzie Jackson****, Morgan Hawker, Kristina Closser,* California State University, Fresno

Plasma enhanced chemical vapor deposition (PECVD) is an attractive method to deposit conformal coatings on surfaces without affecting bulk properties. Current literature showcases PECVD in conjunction with computational studies primarily focused on coating semiconductors with organometallic and semimetal-based films. Many PECVD systems utilize organic precursors to modify surfaces with the goal of interfacing with biological environments. This research seeks to fill the gap by studying the mechanism in which the thin films are deposited using two organic plasma precursors– acrylic acid and pentane. Computational modeling of these organic precursor fragments and how they recombine in the plasma will help in understanding key characteristics of the deposition of the thin film via the thickness of the film, deposition rate, and the chemical composition of the film.

This study models the precursors using two different computational methods: quantum mechanics (QM) and semi-empirical tight-binding (xtb). Feasible fragmentation structures were calculated by hand and modeled with the IQmol molecular viewer for usable cartesian coordinates for later calculations. Density functional theory (DFT) with the B3LYP functional were used to examine geometries, frequencies, and energies of neutral radicals and cations formed during precursor ionization. Data were obtained using the quantum chemistry program Q-Chem along with the 6-311(2d,2p) basis set. Data were then analyzed to determine the most stable fragments, which were subsequently used to predict species most likely formed plasma-polymerized films. Optimized cartesian coordinates from DFT calculations were extracted and utilized for subsequent xtb calculations with the GFN2-xTB method in the meta-dynamics framework to explore most likely structures to 1 degree of polymerization. Data were obtained using the semi-empirical quantum chemistry package Conformer-Rotamer Ensemble Sampling Tool (CREST) that will be further researched to determine the potential chemical composition of the thin film.

6:00pm **PS3-WeA-16 Fully Kinetic Modeling of ICP Chambers Used for Plasma Processing**, ***Daniel Main****, Thomas Jenkins, Scott Kruger, John Cary,* Tech-X Corporation

Low-temperature kinetic plasma simulations using particle-in-cell (PIC) and Monte Carlo methods (DSMC/MCC) for the chemistry can provide many advantages over fluid simulations, including detailed information about the Ion Energy Distribution Function (IEDF) and Ion Angular Distribution Function (IADF) that are critical for plasma processing. In addition, a fully kinetic approach does not make common assumptions made in fluid models, such as local conductivity or Maxwellian distributions of the plasma species. In this talk we present kinetic modeling results of inductively coupled plasmas in a 2D cylindrically symmetric geometry. We demonstrate how implicit methods can make these challenging simulations feasible by reducing computing times by factors of 20-200. We also demonstrate a method of providing constant power to the plasma, which further decreases the runtime needed to achieve steady-state discharges. We then apply DC and/or RF bias voltage below the wafer, introducing capacitive coupling self-consistently into the model to enable better etch control, and explore how steady-state ion fluxes and IEDF/IADFs at the wafer surface vary as a function of RF bias frequency, amplitude, and waveform shape. We show, for example, that a low-frequency CCP bias couples more efficiently with the ions leading to an increase in the RF-averaged ion energy. We also demonstrate that improved IEDF uniformity can be achieved through careful choice of the shape of the bias waveform.

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