Plasma Science and Technology Division
Room A106 - Session PS1-ThA

Plasma-Surface Interactions II

Moderators: Lei Liu, Lam Research Corporation, **Pingshan Luan**, TEL Technology Center America

2:20pm **PS1-ThA-1 A Pseudo-Wet Plasma Etching Mechanism for SiO_2 at Cryogenic Temperature Using Hydrogen Fluoride Gas with*in-Situ* Surface Monitoring***, ***Shih-Nan Hsiao****, M. Sekine,* Nagoya University, Japan*; Y. Iijima, R. Suda, Y. Ohya, Y. Kihara,* Tokyo Electron Ltd., Japan*; T. Tsutsumi, K. Ishikawa,* Nagoya University, Japan*; M. Hori,* nagoya University, Japan

The mainstream of every platform requiring data storage for mobile device applications is the 3D NAND flash memory, which boasts increased data capability. Despite its promising properties, the increasing number of stacking layers to enhance data capability poses various challenges, not only in terms of manufacturing process but also from a fundamental scientific perspective. The intensive development of the stacking number has led to significant advancements in deep hole etching, such as high-aspect-ratio contact (HARC) etching, for the stacking layers. Recently, an ultra-high speed etch process at cryogenic temperature for 3D NAND has been presented [1]. To explore the etching mechanism, the SiO_2 cryogenic etching using hydrogen fluoride (HF) plasma was investigated with *insitu* monitoring techniques including spectroscopic ellipsometry and attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR). A dual frequency capacitively coupled plasma reactor was used to etch the PECVD-prepared SiO_2. The T_s was controlled from 20 to –60 °C by circulating a coolant through the bottom electrode. The etch rate (ER) of the SiO_2 dramatically increased by a factor of approximately 8, from 1.4 to 10.6 nm/s, as T_s was decreased from 20 to –60 °C (see supplemental document for details). The presence of physisorption of HF and H_2O at lower temperature was confirmed by the results obtained using the *in-situ* ATR-FTIR. The absorbance spectra acquired at different T_s clearly display that the HF-related molecules were generated by the HF plasma and absorbed on the surface of the SiO_2 film. The ER exhibiting the increasing trend is consistent with the absorbance intensity of the HF-related molecules (also see supplemental document). This indicates that the absorption of HF and the incorporation of HF-related molecules contribute great impact on etching of SiO_2 at low temperature. Based on these results, a “pseudo-wet” etching model and surface reactions of SiO_2 using HF plasma at low temperature is proposed.

[1] Y. Kihara et al., VLSI symposium T3-22023.

2:40pm **PS1-ThA-2 Coalescence/De-Coalescence Plasma Patterns on a Plasma-Liquid Interface***, ***Jinyu Yang****, O. Dubrovski, P. Rumbach, H. Chang, D. Go,* University of Notre Dame

Self-organized anode patterns in plasma electrolysis have recently gained substantial interest, yet a comprehensive fundamental mechanistic understanding of the pattern formation and self-organization remains elusive. Here, we report observations of a distinct mode consisting of coalescence and de-coalescence oscillations (CDO) between plasma patterns when operating the cathodic glow discharge at a moderate current of ~-26 mA. Fast-imaging measurements resolve a liquid conductivity- and viscosity-dependent CDO frequency of ~200 Hz, indicating a potential transport-limited process as the frequency is far lower than any reaction timescales inherent to plasma processes. We therefore propose that advective transport of liquid phase ions (cations) due to surface capillary waves that arise from the electrostatic Maxwell pressure on the plasma-liquid interface is responsible for the observed CDO plasma patterns. A theoretical model for viscous capillary waves, coupled with the electrostatic Maxwell stress, is developed. Both the theoretical and the experimental data collapse onto a single universal curve, suggesting a strong correlation between the measured CDO frequency and the induced capillary waves. Further experimental investigation using laser-assisted visualization reveals the existence of surface capillary waves when CDO plasma patterns are being generated, confirming the hypothesized connection between the unexpected dynamics of the plasma and the dynamic liquid behavior.

3:00pm **PS1-ThA-3 Plasma-Surface Interactions at Atmospheric Pressure: From Liquids to Catalytic Surfaces***, ***Peter Bruggeman****,* University of Minnesota **INVITED**

The unique non-equilibrium conditions of low temperature atmospheric pressure plasmas enable the delivery of highly reactive plasma species to substrates at (near) ambient temperatures which is beneficial for a broad range of applications. For example, plasmas interfacing with liquids enable plasma-aided decomposition of recalcitrant organic pollutants in water, decontamination of liquids and material synthesis. In addition, the interaction of plasmas with catalysts offers a sustainable electrically driven route to synthesize chemicals such as ammonia, a molecule that is vital for sustaining global food production or can be used to enhance catalytic reactors used for the removal of trace compounds like VOCs and NO_x from polluted air streams.

In this presentation, we will discuss advances in our understanding of the underpinning mechanisms of plasma-induced liquid phase chemistry in the context of plasma-driven liquid phase redox reactions for nanomaterial synthesis and chemical conversions and gas phase plasma-catalyst interactions enabling the formation of NH_3 from N_2 and H_2 at near ambient conditions. We will show that a detailed experimental characterization of well-designed reactors allows us to develop simplified models of the complex plasma-substrate interactions leading not only to a conceptual but also quantitative understanding of the key species involved in the interactions and the rate limiting processes. We will for example show that a detailed knowledge of the gas phase OH and electron densities, allows us to quantitatively explain liquid phase plasma-induced redox reactions [1] and a detailed measurement of gas phase reactive species fluxes to the catalytic substrate enables one to conclude that NH_3 formation by plasma-catalysis is consistent with surface reactions involving N radicals [2].

References

[1] Y. Yue, S. Exarhos, J. Nam, D. Lee, S. Linic, and P. J. Bruggeman, *Plasma Sources Sci. Technol.***31**(2022) 125008

[2] B. Bayer, P. Bruggeman and A. Bhan., *ACS Catal.***13** (2023) 2619-2630

Acknowledgements

This work was partially supported by the US Department of Energy under Award Number DE-SC-0016053, the National Science Foundation under Award Number CBET-2234270 and the Army Research Office under Grant Number W911NF-20-1-0105.

3:40pm **PS1-ThA-5 Enabling Dry Etching of sub-10 Nm Features at Cryogenic Temperature***, S. Srinivasan, J. Li, X. Yang, S. Joshi, T. Liu,* ***Sumit Agarwal****,* Applied Materials, Inc.

As the DRAM density scaling continues, there is an ever-increasing challenge in shrinking pattern space to sub-10 nm to enable higher pattern density. Sub-10 nm features induce considerable challenges for ICP based dry etching since the etching needs to be highly directional and spontaneous chemical etching needs to be minimized. With sub-10 nm space, however, the chemical etching is inevitable at room temperature and we observe tapered profile and top space enlargement even with extensive process optimization. To tackle this challenge, we evaluate carbon and oxide etch at cryogenic temperature, and observe significant improvement. For both carbon and oxide etch, cryogenic temperature was able to improve profile angle, shrink space CD as well as reduce defectivity by orders of magnitude, which were hardly achievable at room temperature. We attribute these improvements to the unique cryogenic temperature regime which have (1) stronger sidewall passivation due to higher radical sticking coefficient, (2) less spontaneous chemical etching due to lower reactivity and (3) unique reaction regime to enable new catalyst and passivation. The higher sticking coefficient at cryogenic temperature also allows leaner chemistry to be used, which reduces passivation at etch front and further increases etch rate and selectivity. We expect these process differentiations will benefit other applications with small features and high aspect ratios as well.

4:00pm **PS1-ThA-6 Study of Nonequilibrium Electron and Vibrational Response During Plasma Excitation***, ***Sara Makarem****, P. Hopkins,* University of Virginia

Plasmas have long been used for the synthesis and manipulation of materials because of their unique ability to deliver both energy and chemically active species to the surface of plasma exposed materials - an attribute that separates them from other approaches to materials processing. Indeed, that feature provides the ability to drive the surface out of thermal equilibrium with the bulk material thus enabling local

physicochemical processes that can be harnessed to establish unique material properties. Traditionally, our understanding of energy delivery from these energetic species is developed using a variety of ancillary plasma diagnostics, temperature measurements, models, and perhaps post-treatment, ex situ surface characterizations to “re-construct” energy deposition and absorption. While certainly of value, none of these approaches provide a direct measure of the localized, transient response associated with the energy flux at the surface.

In this study, with the use of in-situ ultrafast optical detection and sub-picosecond laser systems, we resolve the influence of the various energetic species in an atmospheric plasma on the resulting electronic and thermal response of materials in real time. Through the development of new plasma diagnostics with sub-picosecond to microsecond temporal resolution, we measure the optical response of material surfaces subjected to various types, intensities, and temporal profiles of atmospheric pressure plasma excitations. Through control over both the photon energy and temporal resolution of the laser probe using sub-picosecond and continuous wave lasers of various wavelengths, we selectively probe the optical response of the plasma excited surface, which in turn is related to the electronic structure, scattering dynamics, thermal transport, and elastic and mechanical properties of the lattice. Thus, by utilizing these novel in situ laser-based probes of the electronic, mechanical, and thermal properties of plasma-excited surfaces, we investigate highly non-equilibrium states and properties of materials during plasma exposure.

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