

Plasma Science and Technology Division Room 104A - Session PS+AS+EM+SS-MoM

Plasma-Surface Interactions

Moderators: Yohei Ishii, Hitachi High Technologies America Inc., Erik V. Johnson, LPICM, Ecole Polytechnique, France

8:20am PS+AS+EM+SS-MoM-1 Atomic-scale Numerical Simulation of a Nanometer-Scale Hole Etching of SiO₂ with a Carbon Mask, *Charisse Marie Cagomoc, M Isobe, S Hamaguchi*, Osaka University, Japan

The current generation of mass-produced semiconductor devices uses nanometer-scale technologies to fit millions of transistors in a single chip. However, the demand for higher integration density is still increasing. For example, sub-10 nanometer transistors have been already established for experimental devices, and fabrication technologies of such devices for mass production are now being developed. For nanometer-scale fabrication processes, the granularity of the structure reflecting the finiteness of atomic sizes and the stochasticity of atomic motion may play important roles in determining the final structure. In this study, to understand such atomic-scale effects in nano-scale fabrication processes, we performed molecular dynamics (MD) simulations of etching processes for silicon dioxide (SiO₂) with a carbon mask having a 4-nm diameter hole by energetic fluorocarbon ions. The incident ion energy was typically in the range from 200eV to 1000eV. For example, in the case of CF₃⁺ ion injections, we observed that the depth of the etched out SiO₂ increased with increasing incident ion energy while the channel width became narrower as the etching of SiO₂ went deeper. Tapering of the carbon mask was also observed when the incident ions hit and deform the mask instead of going straight towards the SiO₂. Furthermore, if the incident energy was too high (e.g., 1000 eV in this case), closing of the carbon mask hole occurred due to the formation of long carbon chains that moved across the hole and were bonded to the opposite side. Deposition of carbon atoms from the mask onto the sidewalls of the etched SiO₂ was also observed, which caused the formation of silicon carbide and may have impeded horizontal etching of SiO₂.

8:40am PS+AS+EM+SS-MoM-2 SF₆/O₂ Plasma Nanotexturing of Silicon: Decoupling How Ion Flux and Ion Energy Matter, *Guillaume Fischer¹*, Institut Photovoltaïque d'Île-de-France (IPVF), France; *E DRAHI, S FILONOVICH*, Total SA Renewables, France; *E Johnson*, LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, France

Crystalline silicon (c-Si) solar cell performance can be improved by reducing front surface reflectance. A drastic decrease may be obtained by texturing the surface at the nanoscale ("nanotexturing"), leading to a graded refractive index from air to c-Si. SF₆/O₂ plasma etching of c-Si in a capacitively coupled radiofrequency (CCP-RF) discharge is known to induce spontaneous nanotexturing. This phenomenon – typically resulting in the formation of conical nanostructures (NS) with typical sizes ranging from 30 to 500 nm – occurs through *in-situ* formation of non-volatile inhibitors on the surface. The latter compete with simultaneous physical and chemical etching, and all these mechanisms may be influenced by ion bombardment.

In the present study, the ion energy distribution at the substrate electrode is tuned using Tailored Voltage Waveforms (TVWs) excitation in a reactive ion etching system. TVWs are obtained by adding harmonic frequencies with controlled amplitudes and phase-shifts to the basis driving signal at 13.56 MHz. This technique may give rise to amplitude and slope asymmetries in electronegative plasmas such as the SF₆/O₂ mixture.

Taking advantage of the edge-high total ion flux radial profile on the electrode but with a uniform energy distribution profile, we investigate the influence of both ion energy and ion flux on the nanotexturing process. Process conditions (etching time and driving voltage, i.e. sinusoidal signal or TVWs) are varied, and four samples are simultaneously textured for each set of conditions. The variations in etch rate suggest an ion energy-dependent etching yield. A phenomenological model (etching yield varying with the square root of the ion energy above a threshold at 13 eV) is proposed, and leads to the determination of a clear dependence between the energy weighted ion fluence and the final total hemispherical reflectance of the samples.

This trend is of great relevance for photovoltaic applications, and is explained by the constant increase in NS height during the process, which gradually smoothens the transition of refractive index from air to c-Si.

¹ Coburn & Winters Student Award Finalist

However, the instantaneous ion flux is still observed to influence the aspect ratio (ratio between average height and width of the NS): the higher the ion flux, the higher the aspect ratio. This effect may stem from reduced lateral expansion of inhibitor species on the NS flanks due to the higher ion flux, and will affect the subsequent surface passivation required for photovoltaic applications. Finally, design rules for silicon nanotexturing using SF₆/O₂ plasma are drawn from the observed trends.

9:00am PS+AS+EM+SS-MoM-3 Corrosion Resistance to F and Cl plasma of Yttrium Oxyfluoride (YOF) formed by Sintering, *Akinobu Teramoto, Y Shiba, T Goto*, Tohoku University, Japan; *Y Kishi*, Nippon Yttrium Co., Ltd, Japan; *S Sugawa*, Tohoku University, Japan

Corrosion resistance to the reactive species in some kinds of plasma is very important to construct the reliable semiconductor process equipment. Especially the Fluorine and/or Chlorine plasma have the strong corrosiveness, and then it is strongly required that the inner wall material of the plasma chamber and the components in the plasma chamber have corrosion resistance to them. We have reported the Yttrium oxyfluoride (YOF, Y:O:F=1:1:1) film has the higher resistance to some plasma conditions (N₂/Ar, H₂/Ar, NH₃/Ar, NF₃/Ar, O₂/Ar) than the Y₂O₃ and YF₃ films^{1,2}. In this presentation, we report the corrosion resistance to NF₃/Ar, Cl₂/Ar and O₂/Ar plasma of YOF formed by sintering. The Y, O and F composition was controlled by mixing ratio of the YOF, YF₃, and Y₅O₄F₇ before the sintering, as the results, the O concentration was varied from 3 to 12 %. All YOF formed by the sintering are more stable to NF₃/Ar and O₂/Ar plasma than the YOF film and both Y₂O₃ film and formed by sintering. Cl₂/Ar plasma shows the stronger corrosion effect to the Y₂O₃ and YOF's, however the corrosion resistance to Cl plasma of YOF's is higher than the Y₂O₃.

These results indicate that the YOF is much stable against the corrosion by the plasma, and YOF formed by sintering is the promising material to construct the components in the plasma chamber.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

References

1. Y. Shiba, A. Teramoto, T. Goto, Y. Kishi, Y. Shirai and S. Sugawa, J. Vac. Sci. Technol. A, **35** (2), 021405 (2017).
2. Y. Shiba, A. Teramoto, T. Goto and Y. Kishi, p. 111, AVS 64th International Symp., Tampa, 2017.

9:20am PS+AS+EM+SS-MoM-4 Decay of Hydrogen in NF₃/Ar and O₂/Ar Cleaning Process by Optical Emission Spectroscopy, *Hanyang Li, Y Zhou, V Donnelly*, University of Houston; *J Chiu, X Chen*, MKS

Fluorine atom-generating plasmas are commonly used in many cleaning processes after chambers have been exposed to a variety of etching and deposition reactants and products. The most common feed gas used in these applications is NF₃, due mainly to its ease of dissociation. Repeated processing and chamber cleaning cycles can cause changes in the plasma source, thought to be due mainly to an altering of the nature of the chamber wall protective coatings. In the present study, high power density (5 – 50 W/cm³), low frequency (400 kHz) toroidal inductive plasmas were operated with H₂/Ar (4/96) and N₂/H₂/Ar (3/9/88) feed gases for various periods, alternating with exposure to NF₃/Ar, O₂/Ar, or pure Ar "chamber cleaning" plasmas. H Balmer-alpha optical emission intensity, ratioed to emission from Ar at 750.4 nm, was measured during H₂/Ar exposure and the following cleaning plasma. Hydrogen was detected evolving from the anodized Al plasma source wall coating. The decay of intensity ratio of H/Ar increased with increasing H₂/Ar plasma exposure. NF₃/Ar plasmas enhanced evolution of H, tentatively ascribed to diffusion of F into anodized Al (most likely as F⁻), which reacts with H that would otherwise remain trapped in the layer. The HF product then out-diffuses, leading to plasma dissociation and H emission. Conversely, O₂/Ar plasmas suppressed the evolution of H, presumably because O bonds to Al in anodized Al and ties up hydrogen as bound OH.

9:40am PS+AS+EM+SS-MoM-5 Plasma-surface Interactions in the Strongly Coupled Regime, *Thomas Morgan*, DIFFER, Netherlands **INVITED**

At high fluxes and densities the interaction of a plasma with the walls of its confinement enter the strongly coupled regime [1], where the mean free paths for collisional processes become much smaller than those of the plasma scale size. The surface morphology in such cases may be pushed far out of equilibrium and in turn the recycling and erosion strongly perturbs the near-surface plasma. Such conditions are reached in high flux plasma processing as well as the exhaust region of future large-scale fusion

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reactors such as ITER and DEMO. The linear plasma generator Magnum-PSI [2] is uniquely capable of achieving high density low temperature plasmas with high similarity to fusion reactor exhaust fluxes. Using this device the power handling, long term erosion and evolution of plasma facing materials for ITER and DEMO can be studied, as well as the self-organisation effects and novel structures which occur under such conditions. At plasma-liquid metal interfaces considered as advanced wall components this strong coupling can give rise to vapour shielding of the surface, indicating a novel method to limit heat loading damage to wall surfaces in the reactor exhaust [3]. An overview of results will be given showing how this device is addressing urgent questions for ITER, helping to develop advanced walls for DEMO and beyond, and exploiting non-equilibrium for plasma processing.

[1] A.W. Kleyn et al. *Phys. Chem. Chem. Phys.* 8 (2006) 1761–1774

[2] G. De Temmerman et al. *Fusion Eng. Des.* 88 (2013) 483-487

[3] G.G. van Eden et al. *Phys. Rev. Lett.* 116 (2016) 135002

10:40am **PS+AS+EM+SS-MoM-8 Tailoring the Surface Properties of Porous Zeolite Constructs using Plasma Processing**, *Angela Hanna*¹, *E Fisher*, Colorado State University

Zeolites have been widely used for adsorption, catalysis, and gas separation processes. Despite their extensive use, the ability to control the surface properties of zeolites remains unoptimized. Plasma modification presents an ideal modification methodology with a wide parameter range and the potential to create tailored surface properties and functionalities. Thus, we sought to improve material performance through plasma surface modification, as well as through fabrication of various zeolite constructs (i.e., native zeolites, pellets and electrospun fibers). Moreover, our approach to understand the fundamental plasma chemistry allows us to provide significant insight into mechanisms that will ultimately provide a more thorough evaluation of plasma processing for zeolite surface modification. We employed a range of characterization tools to assess materials before and after plasma treatment and optical spectroscopies to examine the gas-phase of the plasma, both with and without zeolites to evaluate the impact of the material on the gas-phase. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and powder X-ray diffraction were utilized to assess surface chemistry, substrate morphology, and bulk characteristics of the material, respectively, before and after plasma exposure. Water contact goniometry was employed to evaluate the surface wettability, where untreated zeolites were nominally hydrophilic. Here, we explored two fluorocarbon (FC) precursors (i.e., C₂F₆ and C₃F₈) to create more hydrophobic surfaces than the untreated materials. XPS analysis reveals surface fluorination and/or formation of a FC coating on the material. H₂O(*v*) plasmas were also employed to create a more hydrophilic zeolite surface, while maintaining a porous, interconnected network. By also studying the gas-phase, we can glean how the material changes the plasma environment. Species interactions and plasma energetics are intertwined; thus, temporally-resolved data are necessary to accurately probe the intricate dynamics within plasmas. We have investigated formation and destruction mechanisms of key excited state species (i.e., CF, CF₂, OH) to provide mechanistic insight that could be correlated with system energetics data and material properties. Emission spectroscopy was also used to measure the relative gas phase densities of the aforementioned key species as a function of plasma operating parameters (i.e., power, gas mixture, substrate architecture). Our studies have revealed correlations between gas-phase spectroscopic analyses, the gas-surface interface, and the resulting plasma modified surface properties, ultimately leading to improved plasma processes.

11:00am **PS+AS+EM+SS-MoM-9 Generation Kinetics of Plasma-induced Electronic Defects in Semiconductor Materials**, *Shota Nunomura*, *I Sakata*, *K Matsubara*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In state-of-the art semiconductor devices, electronic defects strongly influence the device performance. The electronic defects are often generated during the device fabrication, where a variety of plasma processing technology is used for film deposition, gate etching, dopant implantation and so on. Most defects are recovered by post-annealing, however some defects remain in the devices. Because these defects usually deteriorate the device performance, reduction of these defects is required. However, the kinetics of generation and annihilation of the defects are not fully understood yet.

We studied the kinetics of electronic defects in hydrogenated amorphous silicon (a-Si:H) during H₂ and Ar plasma treatments. The generation and

annihilation of defects are monitored via in-situ photocurrent measurement during the treatment [1-2]. A decrease in the photocurrent indicates the generation of defects whereas an increase in the photocurrent indicates the annihilation of defects. This photocurrent-based monitoring is highly sensitive in the detection of small amount of defect density (~10¹⁶cm⁻³).

The photocurrents in a-Si:H films under various conditions of H₂ and Ar plasma were measured. From the measurements, we find the following [3]. (i) Each plasma treatment immediately causes the generation of defects, indicated by a strong reduction in the photocurrent. (ii) The defects are generated dominantly by the radicals such as hydrogen atoms (H) and argon metastable atoms (Ar*). (iii) The residual defects are created by the bombardment of Ar⁺ ions rather than H₃⁺ ions, radicals and photons. However, the residual defects are recovered mostly by an additional H₂ plasma and post-annealing treatment. (iv) The radicals and photons also generates defects, however these defects are annihilated by the simple post-annealing. The details of the experimental setup, results and discussion are given in the presentation.

This work was supported by JSPS KAKENHI (Grant Number 18K03603 and 15K04717) and NEDO.

[1] S. Nunomura, I. Sakata, and M. Kondo, *Appl. Phys. Express* 6, 126201 (2013). [2] S. Nunomura and I. Sakata, *AIP Advances* 4, 097110 (2014). [3] S. Nunomura et al., submitted.

11:20am **PS+AS+EM+SS-MoM-10 Evolution of Photoresist Layer Structure and Surface Morphology under Fluorocarbon-Based Plasma Exposure**, *Adam Pranda*, *S Gutierrez Razo*, *J Fourkas*, *G Oehrlein*, University of Maryland, College Park

Fluorocarbon-based plasma chemistry is an integral component in enabling the pattern transfer step in the semiconductor manufacturing process. Although significant work has gone towards understand the overall etching behavior, surface roughness, and chemistry development for continuous-wave (CW) plasmas with Ar/fluorocarbon admixtures,¹ a complete understanding of the photoresist layer structure evolution and surface roughness distribution has not been well established. Specifically, under high-energy ion bombardment, a dense amorphous carbon (DAC) layer forms at the surface, impacting the etch resistance and surface roughness. For discrete evaluation of the DAC layer/fluorocarbon interaction, we employed a pulsed plasma setup in which a biased, steady-state Ar plasma was used to develop DAC layers of various thicknesses at the photoresist surface, after which fluorocarbon (C₄F₈) pulses of various lengths were introduced. We sought to answer three key questions: 1. How does the fluorocarbon interaction with the DAC layer impact the layer structure? 2. How is the surface roughness affected by the fluorocarbon interaction? 3. How does the pulsed process compare to a CW Ar/C₄F₈ admixture process?

For sample characterization, we utilized a combination of real-time, *in situ* ellipsometry and X-ray photoelectron spectroscopy at various points during the plasma exposure on an industry-standard 193 nm photoresist, several model polymers, and a 3-color-lithography-compatible photoresist that we are developing. Atomic force microscopy (AFM) was used to monitor the surface roughness evolution and the distribution was calculated using a power spectral density (PSD) analysis.

From the combined analyses, we find that the fluorocarbon depletes the DAC layer by a partial conversion of the surface of the DAC layer into an F-rich mixed layer. Furthermore, the mixing of the fluorocarbon into the DAC layer results in an overall smoothing of the sample surface. By comparing the pulsed process to the CW process, we evaluate the significance of the layer structure in determining the surface behavior in response to variations in fundamental plasma parameters such as the ion energy or exposure time.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309) and the US Department of Energy Office of Fusion Energy Sciences (DE-SC0001939).

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¹ National Student Award Finalist

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11:40am **PS+AS+EM+SS-MoM-11 Fundamental Studies of Plasma Species with Organic Materials of Varying Hydrogen and Oxygen Composition by Computational and Experimental Approaches**, *Yusuke Fukunaga*, Nagoya University, Japan; *P Ventzek, B Lane*, Tokyo Electron America, Inc.; *A Ranjan*, TEL Technology Center America, LLC; *M Sekine, T Tsutsumi, H Kondo, K Ishikawa*, Plasma Nanotechnology Research Center, Japan; *R Upadhyay*, Esgee Technologies; *L L. Raja*, The University of Texas at Austin; *G Hartmann*, McKetta Department of Chemical Engineering, The University of Texas at Austin; *G S. Hwang*, The University of Texas at Austin; *M Hori*, Institute of innovation for future society, Japan

Organic film etching is important for semiconductor device fabrication especially as it relates to self-aligned-multiple-patterning in which sub-nanometer scale pattern replication is critical. Even though the etching of organic materials has been studied for decades (e.g., O₂ plasma ashing), new process applications (e.g. ALE) and new chemistry regimes render older models of organic etching such as those employing the Ohnishi parameter of limited use.[1] Existing kinetic models rely on untested assumptions such as the role of dangling bonds as reaction initiating sites.[2] A need exists to revisit the fundamentals of plasma surface interactions as they pertain to the etching of organic films. Moreover, a need exists to incorporate fundamental kinetic models with macroscale models which could be used for process development.

Progress has been slow because of the computational weight of modeling the chemical kinetics and difficulty defining a tractable problem. In this presentation, we describe the use of an integrated modeling framework involving fundamentals-based ab-initio and plasma chemistry simulations with high performance computing to describe chemical kinetics on model polymer systems. In O₂ and Ar plasmas, we use finite carbon size strands with varying degrees of O, OH or H termination as model structures. For simplicity, the structures are polyethylene-like. We use density functional theory (DFT) to model the interactions between plasma species and representative structures. To estimate the relative importance of plasma species and their energy, we derive species and energy flux from a macroscale plasma chemistry model. Both DFT and ab-initio molecular dynamics (AIMD) simulations are used to probe the chemical stability of representative structures to different plasma species (e.g., Ar, O) and energy fluxes. We found that O addition to H terminated structures results in OH group formation on polyethylene by exothermic reaction. Ar ion bombardment formed carbon strands may also be oxidized. The resultant structures (oxo-carbon) are also stable up to large oxygen to carbon ratios. The stability to Ar ion bombardment will be presented. An essential test of any new mechanism is experimental validation. In addition to the computational results, we will present experimental results ranging from basic etch rate measurements to measurements of plasma processed material chemical composition (e.g., XPS).[3]

References:

[1] H. Gokan, *et al.*, J. Electrochem. Soc.: Solid-state Sci. Technol. **130**, No. 1, 143 (1983).

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