Plasma Science and Technology
Room: A1 - Session PS1-ThA

Fundamentals of Plasma-Surface Interactions II
Moderator: D.J. Economou, University of Houston

2:00pm **PS1-ThA1 Negative Ion Surface Production in Low Pressure Plasma**, ***G. Cartry****, L. Schiesko, J.M. Layet, M. Carrere*, PIIM, Aix - Marseille Université - CNRS, France **INVITED**

Negative ions in plasmas play a main role in the discharge kinetics. For instance they may be at the origin of plasma instability [1], or may be responsible for coalescence in the primary state of dust formation [2]. Plasma based negative ion sources can have many applications. They may be used to reduce surface charge during plasma etching and in the context of controlled fusion research, they are used to generate neutral beams to heat fusion plasma. Therefore controlling negative ion production and loss in plasmas is of primary interest in many research fields. Efficient negative ion sources use caesium deposited on surfaces to increase negative ion production. Indeed, due to its property of reducing the work function, caesium leads to a high negative ion surface production yield. Negative ions are also produced in plasma bulk through electron attachment on molecules. Up to now most of works focused on plasma bulk production and on caesiated-surface production. Few works deal with caesium free surface production while almost all low pressure plasma sources are running without caesium. The aim of the present paper is to study caesium free negative ion surface production in low pressure plasmas.

Our first study is concerned with H2/D2 plasmas and graphite material for fusion applications [3]. However, results obtained here can be extended to low pressure plasma sources used in microelectronic industry for instance, since carbon containing materials are often in interaction with H2 plasmas or even more electronegative plasmas such as oxygen, fluorine or chlorine containing plasmas.

We use a helicon reactor whether in capacitive or inductive mode. A mass spectrometer is placed in the diffusion chamber of the helicon reactor and faces a one square centimetre graphite sample. The sample is negatively biased with respect to the plasma. Positive ions (H+, H2+, H3+) bombards it and negative ions formed (H-) upon bombardment are repelled from the surface toward the plasma. Under low pressure considered here, they reach without any collision the mass spectrometer where they are analysed according to their energy. Study of negatve Ion Distribution Function (IDF) provides information on surface production mechanisms. In this talk we will discuss IDFs measurements, describe how we identify surface production mechanisms, show negative ion surface production yield dependency with positive ion flux and energy, and compare H2 and D2 plasmas.

The authors acknowledge ANR (project ITER-NIS BLAN08-2_310122)

[1] Chabert P et al 2001 Pl. S. Sci. Tech.10 478

[2] Bouchoule A et al 1996 Pure Appl. Chem.68 1121

[3] L Schiesko et al Pl. S. Sci. Tech.17 (2008) 035023

2:40pm **PS1-ThA3 Amorphous Hydrogenated Carbon Etching with a Low Energetic Plasma Jet**, ***T.A.R. Hansen****, J.W. Weber, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, The Netherlands

Structures in the chip industry are approaching the 32 nm half pitch, which requires radiation in the VUV and EUV range. Cracking of hydrocarbon impurities in the vacuum by the radiation causes C growth on the VUV and EUV optics. Each nm of deposited carbon reduces the reflectivity of the optics by 1%. Fast removal of these contamination layers without damage to the underlying optics is essential for the next generation of lithography devices.

Etching with a low energetic plasma jet can be used to selectively remove coatings such as hydrogenated amorphous carbon (*a*-C:H) without damage to the underlying structure. Real time, *in situ* spectroscopic ellipsometry measurements indicate that the highest etch rates are obtained for an Ar/H_2 plasma, rather than for a pure Ar or H_2 plasma.

Even though the etch rate of *a*-C:H thin films is dependent on both temperature and roughness, the highest roughness in absolute values is attained by the plasma with the lowest etch rate. At low temperatures, the etch rate deviates from an Arrhenius relation, while the activation energy is similar for both the H_2 and Ar/H_2 plasma at higher temperatures.

The two orders of magnitude higher etch rate for the Ar/H_2 plasma is due to chemical sputtering, which is a synergistic effect between atomic H and Ar^+ ions with an ion energy below the threshold of 58 eV for physical sputtering. Chemical sputtering has been observed by Hopf et al. for energies above 20 eV and an H to Ar^+ flux ratio over 100 [1]. In our plasma, however, the Ar^+ ion energy is only a few eV's and the estimated H to Ar^+ ratio is lower than 5.

The etch products, released from the surface, consist mainly of CH_4 and C_2H_y, as shown by residual gas analysis. Time resolved optical emission spectra of the Ar/H_2 plasma, from a few mm's in front of an *a*-C:H sample, indicates also the presence of C_2 and CH radicals. The CH radical is formed in the plasma phase through charge transfer between Ar^+ ions and these larger hydrocarbons, and dissociative recombination. Similar plasma chemical processes occur during the remote plasma deposition of *a*-C:H films. However, in contrast with deposition, the CH rotational temperature shows an overpopulation in the higher excited states, indicating that the (internal state of the) parent molecule is different for an etch plasma than for a deposition plasma.

Spatially resolved optical emission measurements are Abel inverted, by means of the numerical Barr method. While there is some CH production throughout the entire plasma jet, the highest CH production occurs in front of the *a*-C:H sample.

[1] C. Hopf, A. von Keudell and W. Jacob, Nucl. Fusion **42** (2002) L27–L30

3:00pm **PS1-ThA4 Investigation of Fluorocarbon PECVD During Processing of Si and ZrO_2 Surfaces**, ***M. Cuddy****, E.R. Fisher*, Colorado State University

Films deposited from fluorocarbon (FC) plasmas exhibit low dielectric constants desirable for interlayers in ultra-large scale integrated circuits (ULSIs). The processing of ULSIs has involved the use of small monomer (CF_4, C_2F_6) FC precursors as an avenue for plasma-enhanced chemical vapor deposition (PECVD). To gain a broader understanding of both the FC plasma system and plasma-surface interactions, we have explored gas phase diagnostics and species-surface reactivity under varying plasma parameters. This presentation will reflect upon data obtained from optical emission spectroscopy (OES) concerning the role of excited state species present in FC plasmas. OES data show that during FC plasma treatment of Si and ZrO_2 wafers, CF_2* concentrations increase independent of feed gas and substrate type. The films deposited from such treatments do, indeed, consist of FC moieties and thus plasma-surface interactions are clearly influential in the overall process. We have studied the interaction of FC plasma species at the interface of depositing films using the imaging of radicals interacting with surfaces (IRIS) technique. IRIS data show that scatter probabilities for the CF_2 radical are greater than unity, indicating that CF_2 is produced from films *at the surface* during FC plasma processing of silicon. Furthermore, we have used quadrupole mass spectrometry to investigate mean ion energies of CF_2^+ in FC plasmas and have discovered that ion energies increase with increasing applied rf power. We have previously demonstrated that IRIS scatter coefficients for CF_2 produced from larger precursors (C_3F_8 and C_4F_8) correlate directly with ion energy. Thus, we will explore the role of this radical during processing of Si and ZrO_2 with small FC precursors as monitored by IRIS studies and compare these results with the respective ion energies for CF_2^+ in these systems.

3:40pm **PS1-ThA6 Studies of Chlorine-Oxygen Plasmas and Evidence for Heterogeneous Formation of ClO and ClO_2**, ***V.M. Donnelly****, J. Guha*, University of Houston

Plasma and surface diagnostics of Cl_2/O_2 mixed-gas inductively coupled plasmas are reported. Using trace rare gas optical emission spectroscopy (TRG-OES) and Langmuir probe analysis, electron temperatures (T_e) and number densities for Cl atoms (n_{Cl}), electrons (n_e), and positive ions were measured as a function of percent O_2 in the feed gas and position in the plasma chamber. Adsorbates on, and products desorbing from a rotating anodized aluminum substrate exposed to the plasma were detected with an Auger electron spectrometer and a quadrupole mass spectrometer. T_e and n_e increased with increasing percent O_2 in the plasma, while n_{Cl} fell off with O_2 addition in a manner reflecting simple dilution. Cl atom recombination probabilities (γ_{Cl}) were measured and were found to be a nearly constant 0.036±0.007 over the range of Cl_2/O_2 mixing ratios and Cl coverage. Large yields of ClO and ClO_2 were found to desorb from the surface during exposure to the plasma, ascribed predominantly to Langmuir-Hinshelwood reactions between adsorbed O and Cl. In addition, the transient surface composition of an anodized aluminum surface was determined as the gas was switched from Cl_2 to O_2 and vice versa. When the surface was first conditioned in an O_2 plasma and then exposed to Cl_2 plasmas, a rapid uptake of Cl was found in the first tens of seconds, followed by a slow approach to a steady state value within ~5 minutes of plasma exposure. Conversely, when the surface was exposed to a Cl_2 plasma for a long time and then switched to an O_2 plasma, the anodized aluminum surface

underwent a rapid de-chlorination in the first few seconds and then a slow approach to steady state over ~3 minutes. The buildup and decay of Cl coverage is well described by a stretched exponential function, reflecting a range of binding sites for Cl. Throughout these treatments, the coverages of Si (from erosion of the quartz discharge tube) and O was nearly constant.

4:00pm **PS1-ThA7 Etching of Silicon and Silicon Oxide in a Pulsed Inductively Coupled Plasma with Chlorine**, ***C. Petit-Etienne,*** LTM/UJF, France, *L. Vallier, E. Pargon, O. Joubert*, LTM/CNRS, France

For the next technological generations of integrated circuits, the traditional challenges faced by etch plasmas (profile control, selectivity, critical dimensions, uniformity, defects, ...) become more and more difficult, intensified by the use of new materials, the limitations of lithography, and the recent introduction of new device structures and integration schemes. Chemical plasma composition can be changed by modifying the gas mixture, ion flux can be partly controlled by source power, and ion energy can be chosen thanks to the bias voltage applied to the substrate. However, these control parameters are not always sufficient to reach all required etching characteristics and new control parameters are needed. Pulsing the plasma source power or the substrate bias offers new operating parameters (pulse frequency, duty cycle). The main advantages of a pulsed etching process are the improvement of etch selectivity and the reduction of charge-up damages and defects by reducing the electron activity and controlling the dissociation of radicals in the plasma.

Studies are being conducted on the etching characteristics of silicon and silicon dioxide in a 300 mm industrial inductively coupled plasma etching chamber having pulsed plasma discharge capability from Applied Materials. The reactor has been modified to be connected to an Angle-Resolved X Ray Photoelectron spectroscopy analyzer by a robotized vacuum chamber. Hence after an etching process, XPS spectra were recorded as function of take-off angle and the integrated intensities of the core-level peaks were used to obtain chlorine concentration and chemical state information from different depths of the sample, thereby permitting non-destructive characterization of chlorine profile in thin silicon oxide films. Material etch rates were measured in real time by in situ multi-wavelength ellipsometry.

When the plasma is pulsed, two parameters can be adjusted, namely the frequency of the pulse and the duty cycle. While the frequency has only a small influence on the etch rates in the investigated frequency range, our results demonstrate that a low duty cycle clearly modifies etch rate and can considerably improve the etch selectivity between silicon and silicon oxide. When a thin silicon gate oxide layer is exposed to very low energy etching conditions, a first step of chlorine incorporation is observed before etching. Preferential accumulation near the SiO_2/Si interface is observed and chlorine is shown to bond to both silicon and oxygen in multiple distinct chemical states.

4:20pm **PS1-ThA8 Fully Atomistic Profile Evolution Simulation of Nanometer-scale Si Trench Etching by Energetic F, Cl, and Br Beams**, ***H. Tsuda****, T. Nagaoka, K. Eriguchi, K. Ono,* Kyoto University, Japan*, H. Ohta*, University of California, Santa Barbara

An atomic-scale understanding of interactions between chemically reactive plasmas and surfaces is required to establish nanometer-scale processing technologies. Various numerical studies based on molecular dynamics (MD) simulation have been reported so far, but these were limited to simulations of the simple blanket etching to estimate microscopic etching properties [1,2]. Here, we first report a fully atomistic silicon feature profile simulation using classical MD simulations. The potential form can be found in our previous papers [2,3,4]. F, Cl, and Br beams with a translational energy of 100 eV were used as reactive species. The surface area of Si (100) substrates was about 163 × 22 $Å^2$, where 3840 silicon atoms were initially located in the structure of diamond lattice. M ask patterns were introduced in the direction parallel to the short axis with periodic condition, in order to reproduce the trench etching feature. Then, the area without mask was 50 × 22 $Å^2$. By using our new atomistic profile evolution simulation, we investigated halogen plasma-surface interactions at sidewalls and bottom surfaces of nanometer-scale Si trench in detail. It was found that specific feature profiles with different gaseous species appear not only at the sub-micrometer-scale but also at the nanometer-scale etching, and the difference of surface reaction layer formation strongly affects the feature profile evolution during etching. For instance, fluorine beam etching showed that fluoride layer is formed on the entire surfaces containing sidewalls and bottom surfaces, thus giving isotropic etching. Chloride layer was thicker than fluoride and bromide layers, to give feature profiles of sidewall tapering. Bromide layer on bottom surfaces was thinnest among the three, and so the etching rate was lowest. So, it was cleared that the surface reaction layer formation strongly affects the feature profile evolution during etching. Our approach is essential as a reference for macroscopic or empirical profile simulation, where simulation sizes have been reduced recently. We also show some comparison between MD-based profile simulation and our empirical profile simulation (atomic-scale cellular model [5]).

[1] H. Ohta *et al*., J. Vac. Sci. Technol. A **19**, 2373 (2001).

[2] T. Nagaoka *et al*., J. Appl. Phys. **105**, 023302 (2009).

[3] H. Ohta and S. Hamaguchi, J. Chem. Phys. **115**, 6679 (2001).

[4] H. Ohta *et al*., J. Appl. Phys. **48**, 020225 (2009).

[5] Y. Osano and K. Ono, J. Vac. Sci. Technol. B **26**, 1425 (2008).

4:40pm **PS1-ThA9 Molecular Dynamics Simulations of Oxygen-Containing Polymer Sputtering and the Ohnishi Parameter**, ***G.K. Choudhary****, J.J. Végh, D.B. Graves*, University of California, Berkeley

The effects of ion bombardment on polymer surfaces can be profound, with implications for all plasma-based pattern transfer processes that involve the use of polymer etch masks in lithography and etching. It is known that Ar^+ bombardment of various polymers results in the formation of a 1-2 nm deep cross-linked region at the exposed surface, and that virgin polymer sputtering yields can be several orders of magnitude higher than steady state yields after ion bombardment. [1]

In this talk, we report results from molecular dynamics (MD) simulations of Ar+ (~ 40 - 150 eV) sputtering of oxygen-containing polymers. The MD data are compared to available experimental results, with special focus on the so-called Ohnishi parameter, which has been shown to correlate with sputtering yields for many O-containing polymers. [2] The MD simulations match the published correlations well, and we present a quantitative model of sputtering for these polymers that shows why the Ohnishi parameter (a function of the polymer composition) is proportional to the steady state sputtering yield.

However, we also show that the Ohnishi parameter does not correlate with yields for other polymers, including polyfluoroethylene and polyethylene. The MD simulations show that the validity of this parameterization is dependent on whether or not the sputtering of the polymer transitions between ion-induced scissioning to cross-linking at steady-state.

Finally, we discuss the implications of the dynamics of ion-induced surface cross-linking for synergistic photoresist roughening that occurs in plasmas, especially in the presence of vacuum ultraviolet photon and/or beaming electron exposure.

[1] J. J. *Végh, D. Nest, D. B. Graves et al. " Near-surface modification of polystyrene by Ar+: molecular dynamics simulations and experimental validation" Applied Physics Letter, vol. 91, pp. 233113-1-3, 2007.*

[2] H. Gokan, S. Esho, and Y. Ohnishi, "Dry etch resistance of organic materials," J. EZectrochem. SOC., vol. 130, pp. 143-146, 1983.

5:00pm **PS1-ThA10 Charge Trapping and Valence-band Structure of VUV-Irradiated BEOL Dielectrics**, ***J.L. Lauer****, J.L. Shohet,* University of Wisconsin-Madison*, Y. Nishi,* Stanford University*, A. Antonelli*, Novellus Corporatiion

The minimum spacing between conductive lines in advanced integrated circuits (ICs) continues to decrease with each generation of technology. As a result, the long-term reliability of ICs is becoming increasingly dependent on the reliability of the intermetal dielectrics which often become damaged during back-end-of-the-line (BEOL) processing. Dielectrics used in BEOL structures are often irradiated with photons of various energies during plasma processing, charge annealing, and curing of porous materials. In particular, processing plasmas produce significant amounts of vacuum ultraviolet (VUV) radiation which are, among other processes, capable of creating electron-hole pairs within dielectrics. As a result, VUV radiation has an impact on the electrical conductivity of dielectrics during plasma processing which can either contribute to or mitigate trapped charge within dielectrics. We compare the charging response of 50, 250, and 450 nm of SiOCH, SiN, SiCO, SiCN, and SiC dielectrics on Si substrates after irradiation to vacuum ultraviolet (VUV) radiation. We choose to irradiate the dielectric layers to a photon energy of 9.5 eV because photons with this energy are often emitted from processing plasmas that contain oxygen, i.e. ashing and etching plasmas. The charging response of the dielectrics was evaluated by measuring the surface potential on the dielectrics with a Kelvin probe after irradiation with several doses of 9.5 eV photons. The surface potential on all of the dielectrics after VUV irradiation was positive due to the accumulation of positive charge by traps located within the dielectrics. By comparing the surface potential on several thicknesses of dielectrics after VUV irradiation we can estimate the location within the dielectric the charge is trapped. The surface potential on SiOCH layers of varying k-values after VUV irradiation indicates the presence of both negative- and positive-charged traps. From VUV-spectroscopy, we determined the SiOCH layers have electron traps located 0.8 eV below the conduction-band edge and hole traps located 1.4 eV above the valence-band edge.

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Authors Index

Bold page numbers indicate the presenter

— A —

Antonelli, A.: PS1-ThA10, 2

— C —

Carrere, M.: PS1-ThA1, 1
Cartry, G.: PS1-ThA1, **1**
Choudhary, G.K.: PS1-ThA9, **2**
Cuddy, M.: PS1-ThA4, **1**

— D —

Donnelly, V.M.: PS1-ThA6, **1**

— E —

Engeln, R.: PS1-ThA3, 1
Eriguchi, K.: PS1-ThA8, 2

— F —

Fisher, E.R.: PS1-ThA4, 1

— G —

Graves, D.B.: PS1-ThA9, 2
Guha, J.: PS1-ThA6, 1

— H —

Hansen, T.A.R.: PS1-ThA3, **1**

— J —

Joubert, O.: PS1-ThA7, 2

— L —

Lauer, J.L.: PS1-ThA10, **2**
Layet, J.M.: PS1-ThA1, 1

— N —

Nagaoka, T.: PS1-ThA8, 2
Nishi, Y.: PS1-ThA10, 2

— O —

Ohta, H.: PS1-ThA8, 2
Ono, K.: PS1-ThA8, 2

— P —

Pargon, E.: PS1-ThA7, 2
Petit-Etienne, C.: PS1-ThA7, **2**

— S —

Schiesko, L.: PS1-ThA1, 1
Shohet, J.L.: PS1-ThA10, 2

— T —

Tsuda, H.: PS1-ThA8, **2**

— V —

Vallier, L.: PS1-ThA7, 2
van de Sanden, M.C.M.: PS1-ThA3, 1
Végh, J.J.: PS1-ThA9, 2

— W —

Weber, J.W.: PS1-ThA3, 1