Plasma Science and Technology
Room: 25 - Session PS2-WeA

Plasma Surface Interactions during PECVD and Plasma Surface Modification
Moderator: C.A. Wolden, Colorado School of Mines

2:00pm **PS2-WeA1 Surface Modifications Induced by Extreme Fluxes of Low-Energy Ions**, ***G. De Temmerman***, *K. Bystrov,* FOM Institute DIFFER, Netherlands, *M.J. Baldwin, R.P. Doerner,* University of California San Diego, *L. Marot,* University of Basel, Switzerland, *H.Y. Xu,* Tsinghua University, China, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands **INVITED**

The interaction of energetic particles with solid surfaces is at the core of numerous applications such as thin film deposition or materials processing. Ion-beam processing, for example, allows nanostructure formation on metal and semiconductor surfaces, while reactive ions can be used to chemically modify surfaces during nitriding for example. Those processes usually involve ions with energies above 100eV where ion-induced damage creation and physical sputtering are expected, and are relatively well documented. In a fusion reactor, at locations where the plasma intersects with the solid surfaces, plasma-facing surfaces are bombarded by extreme particle fluxes (up to $10^{24}m^{-2}s^{-1}$ or $1.6x10^{5}A.m^{-2}$), albeit with energies below 50eV. While the ion energy is below the damage threshold for the incoming ions, the particle flux is high enough to cause a local supersaturation of mobile gas particles within the implantation zone and strong surface morphology changes as a result of cluster/bubble growth.

Combining a high efficiency plasma source and a strong magnetic field, linear plasma devices (LPD) can generate such high ion fluxes and allow fundamental studies of plasma-induced surface modifications under high heat and particle fluxes. The effect of high fluxes of hydrogen, helium and neon ions on metal surfaces, such as tungsten, has been investigated over a wide range of surface temperatures (300-2000C) and ion energies (10-50eV). In all cases, the surface modifications depend strongly on these two parameters, which control the near-surface particle trapping and material properties (mechanical properties, self-diffusion).

Nanostructuring of the surface through formations of ripples or nanoscopic voids is observed for hydrogen irradiation. In the case of helium, a fibreform nanostructure is formed with a typical size in the range 20-1000nm depending on the surface temperature. For neon ions, both a fine-scale ripple structure and large blisters are observed on the surface.

An overview of these results will be given with an emphasis on the surface properties and the application of low-energy ion fluxes as a surface processing technique.

2:40pm **PS2-WeA3 Investigation of Plasma-Surface Interactions Between Hydrogen Radical and Chemically Amplified Photoresist**, ***A. Malinowski***, Institute of Electron Technology, Poland, *M. Sekine, M. Hori, K. Ishikawa, H. Kondo, T. Takeuchi, T. Suzuki,* Nagoya University, Japan, *A. Jakubowski, L. Lukasiak,* Warsaw University of Technology, Poland, *D. Tomaszewski*, Institute of Electron Technology, Poland

As FinFET transistors become necessary, FEOL etch processes will become much more challenging, bringing new constraints to etch selectivity, anisotropy, and etch damage. System-on-a-chip RF and analog devices may have double and triple gates and can be subjected to 12 or more photoresist (PR) removals. Thus development damage-less PR removal is critical for reducing plasma induced transistor electrical parameters fluctuations. In addition to poor uniformity or heavy environmental burden, hydrogen radical-based PR removal is expected to overcome critical problem of damage to the device inborn to currently used PR removal based on oxygen plasmas. As double and “multi” ArF 193nm patterning solutions continue to be a significant vehicle for extending Moore’s Law, it is imperative to investigate plasma-surface interactions between hydrogen radical and chemically amplified ArF 193nm PR. The key element from point of view of etch reaction process kinetics investigation is radical sticking coefficient (SC).

In our study we have developed novel technique for radical SC estimation based on processing of PAPE structure (PAllet for Plasma Evaluation) followed by numerical simulation. Our approach is based on normalized profiles matching of etched PR thickness on parallel plate after PAPE structure processing, using hydrogen high density radical source, with simulated profile of number of stuck radicals on the same plate.

Understanding of the interactions of atomic hydrogen with ArF 193nm PR surface is of both fundamental and technological interest thus recombination mechanism of hydrogen atom on PR surface must be considered. In our approach SC is a sum of etch probability (EP) and recombination probability (RP) and estimated values of EP (0.07) and RP (0.1) reveal fact that recombination dominates during PR etching by hydrogen. Since recombination lowers the number of radicals that are bound to the surface, the reactive species coverage is reduced by this process. Dominance of recombination in conjunction with very low value of EP itself explains very low etch rate, which is on the order of a few nm per minute (it was 3.8 nm/min). In addition similarity of RP obtained in this study and Koleske et al. reveals that the recombination is the result of a gas phase atom abstracting an atom of the same type that has previously chemisorbed to the surface according to the Eley-Rideal mechanism.

Inefficiency of the kinetic energy loss by hydrogen radicals during the PR surface collision, by means of phonon excitation or momentum transfer explains very low value of EP (0.07). Increase of temperature (323 K) of the structure involved proportional increase of EP (0.09).

3:00pm **PS2-WeA4 Kinetic Theory of the Sheath near Electron Emitting Surfaces**, ***J.P. Sheehan***, University of Wisconsin Madison, *I.D. Kaganovich,* Princeton Plasma Physics Laboratory, *N. Hershkowitz,* University of Wisconsin Madison, *Y. Raitses*, Princeton Plasma Physics Laboratory

It has long been known that electron emission from a surface significantly affects the sheath surrounding that surface. Typical fluid theory of a planar sheath with emitted electrons assumes that the plasma electrons follow the Boltzmann relation and the emitted electrons have zero energy at the surface and predicts a potential drop of 1.03 T_e across the sheath when the surface is allowed to float. By removing the assumption that all plasma electrons entering the sheath are reflected back into the bulk plasma (i.e. the Boltzmann relation) and considering those electrons lost to the wall, the predicted sheath potential is reduced to 0.91 T_e. Analysis of this type has been published by various authors, but our work presents a more accurate model. We performed an analytical study of sheath and presheath structure making use of a kinetic description of the emitted and plasma electron densities in the self-consistent electric field. It is shown that kinetic theory predicts that the sheath potential depends on the ratio of temperatures of plasma and emitted electrons (Θ_e). For Θ_e = 5 (for example, for 0.2 eV emitted electron temperature and 1.0 eV plasma electron temperature), theory predicts a sheath potential of half that predicted by fluid theory. The effects of a bi-Maxwellian Electron Energy Distribution Function (EEDF) were considered. These predictions were compared to measurements made in a non-magnetized plasma confined by a multidipole chamber which has a bi-Maxwellian EEDF. A barium-tungsten dispenser cathode was used as a planar emitted electron source. The inflection point in the limit of zero emission emissive probe technique was used to measure the plasma potential in the sheath and presheath near the emitting surface. These results were compared to the kinetic theory and the effects of the bi-Maxwellian EEDF were taken into account.

4:00pm **PS2-WeA7 Probing CF and CF_2 Surface Reactivities in Inductively-Coupled Fluorocarbon Plasmas**, ***M.F. Cuddy****, *E.R. Fisher*, Colorado State University

Inductively-coupled fluorocarbon plasmas (FCPs) provide a wide range of potential applications from circuitry fabrication to preparation of optical coatings. In these systems, etching and deposition processes often occur simultaneously, with the net effect of surface processing dictated by the balance between the two phenomena. The behavior of CF_x (x=1,2) species in particular provide insight into these competing processes and allow for elucidation of the mechanisms of FCP processing. We have examined CF_x radical scatter coefficients (*S*) at the gas-surface interface for a range of FCPs during plasma-enhanced chemical vapor deposition (PECVD). Our imaging of radicals interacting with surfaces (IRIS) experiments reveal that CF and CF_2 species scatter from surfaces with a high probability in each of the systems investigated. These high scatter values are related to the ion energies of nascent plasma species, as measured by mass spectrometry. Highly energetic ions ablate fluorocarbon passivation layers to extricate CF_x units. The presence of vibrationally hot $CF(^2\Delta)$ radicals correlates directly with increasing scatter values for $CF(^2\Pi)$, suggesting that internal energy transfer at surfaces is another important factor contributing to the observed *S*. The connection between interfacial interactions and the PECVD-deposited film is a critical component to consider for improved plasma applications and for designing specificity in fluorocarbon film properties. Ultimately, by controlling the parameters associated with our plasma systems, we can create tailored films with specific compositions and surface

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energies. The efforts recounted here offer additional insight into the fundamental plasma processes so crucial for advancement of plasma technology.

4:20pm **PS2-WeA8 Effects of Ar Ion Bombardment on Protection of Organosilicate Glass from O_2 Plasma Damage**, ***H.Ur. Kazi***, *S. Gaddam, J.A. Kelber*, University of North Texas

In-situ XPS studies of Ar ion bombardment on organosilicate glass (OSG) films at ion kinetic energies between 500eV and 900eV demonstrate that such bombardment inhibits O2 plasma-induced carbon loss by forming an SiO2-like overlayer, and that the degree of protection correlates directly with increased ion energies, but not the thickness of SiO2 overlayer. Bombardment at 500eV results in a ~3 Å thick SiO2overlayer and subsequent O2 plasma treatment results in a slower rate of carbon loss from the surface region than observed for a vicinal film, but complete carbon removal is observed after 3 min O2plasma treatment under these conditions. In contrast, bombardment by a similar flux of 900eV ions results in a SiO2-like overlayer of similar average thickness, but with greatly inhibited rate of carbon loss upon subsequent O2 plasma exposure. Ar ion bombardment (900eV) in the presence of NH3 (1 x 10-6 Torr) results exclusively in Si-N rather than C-N bond formation, and dramatically increases the average thickness of the Si-O-N overlayer to 22 Å. The formation of this overlayer further reduces the rate of subsequent O2 plasma-induced carbon loss compared to 900eV Ar ions alone. These results indicate Ar ion bombardment causes Si-C bond scission. Subsequent NH3 reaction results in Si-N bond formation and inhibits Si-Si and Si-O-Si formation, increasing the thickness of the ion-induced damage overlayer. The data indicate that ion kinetic energies are a critical parameter in protective noble gas plasma treatments to inhibit O2 plasma damage, and also indicate that high energy ions alone can provide better protection against carbon loss when compared to plasmas or VUV photons.

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4:40pm **PS2-WeA9 Ion-Surface Interaction during Microcrystalline Silicon Thin Film Growth**, ***J. Palmans***, *A.C. Bronneberg, X. Kang, M.C.M. van de Sanden, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, the Netherlands

Thin-film silicon solar cells extensively use hydrogenated microcrystalline silicon (μc-Si:H) where large area and fast deposition processes are considered key issues. Both requirements can be fulfilled when operating in the so-called high pressure depletion (HPD) regime in a parallel plate capacitively coupled plasma (CCP). This latter involves high plasma powers (~0.5 W/cm^2), enabling high growth rates through high silane (SiH_4) depletion, and high pressures (> 0.75 Torr) enhancing the material properties by suppressing the ion bombardment. In this work direct ion measurements obtained in a parallel plate CCP are presented for two collisional pressure regimes enabling a quantitative comparison of the role of ions during the plasma-surface interaction and its relation to the amorphous-to-microcrystalline silicon phase transition as determined in both the HPD (10.50 Torr) and a low pressure (0.45 Torr) regime by varying the SiH_4 flow rate, while preserving hydrogen (H_2) flow rate and power density. By relating Raman and infrared absorption spectroscopy data the absence of the narrow high stretching modes and oxidation processes for the solar-grade μc-Si:H thin films has been demonstrated. Next to material analysis, this contribution will address selected aspects of plasma-surface interaction during μc-Si:H deposition. A capacitive probe has been implemented to study the ion flux for a range of parameters, i.e. silane flow rate and plasma power, whereas ion energies are determined with a retarding field energy analyzer (limited to pressures < 0.75 Torr), both implemented in the substrate holder. In the HPD regime an increase of SiH_4 flow rate (0-10 sccm) is found to induce only a moderate increase in ion flux, accounting for 30% of the growth flux for solar-grade material [1]. With ion energies limited to below 19 eV (in collisionless H_2 plasma), less than 6 eV are estimated to be available per deposited Si atom, suggesting that we are either in a regime of Si surface atom displacement, or more likely that a thermal spike is induced at the surface by the arrival of ions, enhancing the radical surface diffusion. Since the ion energy measurements are compatible only with low pressure, this study supports the direct correlation between material quality and plasma-surface interaction in terms of ion energy. The novel insights obtained can lead to the further development of deposition techniques in order to meet the stringent requirements of solar cells in terms of efficiency and production costs.

[1] A.C. Bronneberg, X. Kang, J. Palmans, P.H.J. Janssen, T. Lorne, M.C.M. van de Sanden and M. Creatore,

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5:00pm **PS2-WeA10 Time Resolved Characterization of Pulsed ICP CH_4 – H_2 Based Plasmas**, *S. Jacq,* ***L. Le Brizoual***, *C. Cardinaud, A. Granier*, University of Nantes - CNRS, France

Pulsed rf plasmas are increasingly being employed for plasma etching or deposition. In the case of etching, as the semiconductor feature sizes decreases and feature density increases, the industry is facing the increasing challenge of finding new plasma processes for the requirement of the next devices generation. CH_4-H_2 based plasmas are widely used for dry etching of II-VI and III-V semiconductors. Pulsed plasmas combined to time resolved measurements are known to be powerful tools to study species kinetics. In this study, pulsed CH_4-H_2 plasmas created in a low pressure inductively coupled rf plasma (ICP) are analyzed by time resolved optical emission spectroscopy (TR-OES), mass spectrometry (TR-MS) and electrostatic probe measurements. Plasma conditions are the following: 800 or 1000 W RF power, 20 mTorr pressure, 5 to 50 ms period and 10 to 50 %duty cycle. A cylindrical Langmuir probe and a planar probe are used to measure the electron density (n_e), electron temperature (T_e) and ion flux density. The species creation kinetics is investigated by TR-OES. Since no emission occurs during the off time (n_e and T_e decreases drastically), the double pulse technique is used with a probing pulse time of 0.75 ms. This communication is focused on pseudo-actinometry for the kinetics of H atoms and radicals (CH..). Mass spectrometry is carried out with a time resolved and energy-resolved mass spectrometer on CH_3. For TR-MS, the transit times in the apparatus are calculated for each ion.

During the post-discharge, the decay characteristic time is below 1 ms for H atom density. The time evolution of ne over one period reveals that ne needs 1 ms to reach a stationary state and decreases with a characteristic time of about 0.1 ms. However, the decrease time of Te seems to be shorter than 0.1 ms. Although the H atom kinetics is very fast, and characterized by a decay time below 1 ms, it is slower than the time evolution of n_e and T_e. However, considering the diffusion coefficient of H atoms in the various gas mixtures, different rise and decrease characteristic times could indicate different reaction probabilities on the walls, in relation with the gas mixture. Characteristic times and associated reaction probabilities, using Chantry's formalism are determined to be equal to 0.52 ms (on time) 0.80 ms (off time) which corresponds to H loss probability γ_{on}=0.3 and γ_{off}=0.1. Similar mass spectrometry measurement on CH3 plasma species will be presented. Influence of ion bombardment on the H loss rate at the chamber walls is discussed and this seems to be the key point for chamber conditioning in the pulsed mode.

5:20pm **PS2-WeA11 Plasma-Surface Interactions, Erosion, and Impact on Plasma Distribution Functions**, ***N. Fox-Lyon***, University of Maryland, College Park, *D.B. Graves,* University of California Berkeley, *S.Y. Moon, V.M. Donnelly, D.J. Economou,* University of Houston, *G.S. Oehrlein*, University of Maryland, College Park

Plasma-surface interactions can play a large role in changing characteristic plasma distribution functions. To improve our fundamental understanding of these effects, we leverage several plasma characterization techniques (Langmuir probe, ion energy/mass analyzer, optical emission spectroscopy) with real-time characterization by *in situ* ellipsometry of the eroding plasma-facing surface. Using these methods, we qualitatively and quantitatively studied the time evolution of gaseous and surface derived plasma impurities. High-density inert plasmas (Ar) and low-density reactive plasmas (H_2, D_2) respond differently to molecular impurities in the plasma. When H_2/D_2 or surface/gaseous derived CH_X -related impurities are introduced into Ar plasma, large changes in plasma properties are observed. We report on changes to the ion energy/mass distributions, electron temperature/distribution functions, and plasma density for different conditions . CH_X effects on H_2 and D_2 plasmas, and H_2/D_2 plasma mixtures were also investigated. We also explore the effects of changing the relative C:H fluxes into the plasma from eroding surfaces using graphitic (high C:H ratio) and polymeric (lower C:H ratio) films. In steady-state contact with plasmas, hydrocarbons are eroded as C, H, and CH_X impurities into the plasma reflective of their initial C:H ratios. Along with these studies, we have compared how varying the gap distance between the plasma generation coil and hydrocarbon substrate electrode affects impurity fluxes and plasma properties. A comparison of plasma properties for two different inductively coupled plasma reactors has also been completed and sheds light on how plasma properties and observed trends change for different geometries and plasma sources.

5:40pm **PS2-WeA12 MD Simulations of Hydrogen Plasma Interaction with Graphene Surfaces**, ***E. Despiau-Pujo***, *A. Davydova, G. Cunge,* CNRS/UJF-Grenoble1/CEA LTM, France, *L. Magaud,* CNRS/UJF Institut Neel, France, *D.B. Graves*, University of California Berkeley

Due to its unique 2D structure and its outstanding physical, chemical and mechanical properties, graphene is a promising candidate for a large number of novel applications in microelectronics, for transparent conducting electrodes, sensors or energy storage devices. The successful

development of graphene-based technologies relies on the capability to grow and integrate this new material into sophisticated devices but the nm-scale control of graphene processing overwhelms current based-plasma technology. Therefore, innovative technological steps have to be developed to allow the growth of graphene layers on large areas wafers and their patterning using conventional lithography and plasma etching schemes.

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous-wave plasma processes are not able to selectively etch ultrathin films without damaging the active layers of nanoelectronic devices. In order to achieve uniform/smooth patterning, doping or chemical modification of graphene films without damaging the substrates, one possible alternative is to use pulsed-plasma discharges which exhibit lower average ion energies (thus minimizing surface damage) and are promising to achieve sub-nm thick layers etching. However, the interactions between reactive pulsed plasmas and surfaces are so complex that the efficient development of new processes requires numerical simulations. Therefore, we propose to develop Molecular Dynamics (MD) simulations to understand the role of ion energy in plasma-graphene interaction and to determine the relationship between the flux/energy of reactive species (ions, radicals) bombarding the surface and its structural/chemical modifications.

In this paper, we investigate the interaction between hydrogen plasma species and single/multilayer graphene samples via MD simulations. C-H interatomic potential curves and associated energy barriers are reported depending on the H impact position (top, bridge, hollow or edge sites of GNRs). The influence of graphene temperature and incident species energy on adsorption, reflection and penetration mechanisms is presented. Except for impacts at GNRs edges or at defects location, H species are shown to experience a repulsive force due to delocalized π-electrons which prevents any species with less than ~ 0.7eV to adsorb on the graphene surface. It also appears that the chemical binding of H to sp2-C requires a local rehybridization from sp2 to sp3 resulting in structural changes of the graphene sample. H^+ bombardment of ABA- and ABC-stacked multilayer graphene sheets are compared and the possibility to store hydrogen between consecutive layers is discussed.

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