Plasma Science and Technology
Room: Aztec - Session PS1-WeA

Plasma Surface Interactions (Fundamentals & Applications) II
Moderator: J. Guha, Lam Research Corporation

2:00pm **PS1-WeA1 VUV-Induced Bond Scission and Site-Specific Nitridation in Organosilicate Glass: Bulk and Surface Effects**, ***S. Behera****, University of North Texas, *J. Lee,* University of California-Berkeley, *S. Gaddam, S. Pokharel,* University of North Texas, *D.B. Graves,* University of California-Berkeley, *J.A. Kelber*, University of North Texas

In-situ XPS and ex-situ FTIR have been used to characterized the effects of ionizing vacuum ultraviolet (VUV— 147 nm) photons on the surface composition of organosilicate glass (OSG; k = 3.0). VUV irradiation is an important component of the plasma environment, and both the types and kinetics of VUV- induced effects must be understood in order to accurately control and model plasma effects. Irradiation was carried out in vacuum (10^{-6} Torr), and in the presence of 10^{-4} Torr NH_3 so that NH_3 reactions with VUV-induced reactive sites would cause chemical shifts in XPS core level spectra, permitting a more detailed characterization of photo-induced chemistry. The effects of photo-excited gas phase species are negligible under these conditions, as confirmed by experiments with the light path parallel to the surface. FTIR and XPS data after photoirradiation in vacuum indicate photon-induced Si-C and Si-O bond scission. Lifetimes of bulk Si reactive sites are ~ 6 days, as determined by Si-OH, but ~ minutes at surface sites due to reaction with chamber ambient. Core level XPS spectra recorded after irradiation in the presence of NH_3 show similar effects, but with nitridation at Si sites, and not at carbon sites. Si-C/Si-O bond breaking and C-C bond formation obey first order kinetics. At longer exposure times, the nitridation process saturates while the Si-C/Si-O bond scission and C-C bond formation processes do not, consistent with photo-induced surface densification inhibiting NH_3 diffusion into the solid. However, similar increases in surface carbon intensity were observed for photoirradiation of SiO_2 with ~ 1 monolayer of surface carbon, indicating that reaction of background gases with surface reactive sites may also be a factor. Preferential Si-N bond formation and absence of C-N bond formation were also reported[1] for OSG bombardment by Ar^+ in the presence of NH_3 and suggest fundamentally different dissociation pathways/kinetics at Si vs. C sites created by either ion bombardment or ionizing photoirradiation. C-C and C-H bond dissociation enthalpies are larger than those of Si-H or Si-C bonds, but smaller than that of Si-O, so this site specificity is not readily explainable on the basis of bond strengths alone.

[1]J. A. Wilks and J. A. Kelber, Applied Surface Science **255** (2009) 9543

Acknowledgements: This research was supported by the Semiconductor Research Corporation under Task IDs 1862.001 and 1862.002.

2:20pm **PS1-WeA2 Real-time Measurements of Material Modifications by VUV Radiation during Plasma Etching of 193nm PR**, ***F. Weilnboeck**, R. Bruce, G.S. Oehrlein,* University of Maryland, *T.-Y. Chung, D.B. Graves,* University of California, Berkeley, *M. Li, D. Wang,* Dow Electronic Materials, *E.A. Hudson*, Lam Research Corporation

Plasma radiation in the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral range is a fundamental component of plasma processes used for pattern transfer of nanometer structures. Photons in this wavelength range can lead to severe modification of photoresist (PR) materials in depths exceeding 100nm. We studied the material modifications of fully formulated 193nm PR by plasma photon radiation in Ar plasma discharges. A novel filter approach was applied allowing to probe PR surface modifications in real time by *in-situ* ellipsometry during plasma processing while protecting the PR against ion bombardment. Different filter materials enable to test dependencies on wavelength ranges of the plasma radiation from visible to VUV light. Material modifications were also characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. By combining these data with optical multilayer ellipsometric simulations, material thickness reduction and changes in optical properties could be understood on a molecular level.

Radiation in the UV/VUV spectral range was found to modify the PR at a depth of ~100nm leading to thickness reduction of up to 12nm, whereas radiation in the VIS spectral range modifies the entire film (~400nm) leading to marginal changes in the film thickness. The thickness reduction is caused by material loss, mainly by detachment and loss of lactone, and to a larger extent by densification of up to 9% following the detachment of the PR pendant groups.

Radiation exposure also leads to a change in film optical properties which is discussed in terms of a bond polarizability model. This enables correlation of the measured data with changes of the PR structure on a molecular level. For exposure of the PR to UV/VUV radiation it was found that besides loss of lactone and detachment of the PR pendant groups a significant amount of C-C bonds were lost which can be directly correlated to changes in the polymer structure by chain scissioning reactions.

Real time measurements allow for extracting the temporal evolution of material removal, densification and changes in film optical properties as a function of photon flux and degree of modification. It was found that material modification can be separated into two fundamentally different regimes. In the initial exposure period to plasma radiation in the UV/VUV spectral range changes in film properties are rapid and mainly limited by the photon flux. For extended exposure times modification is flux dependent but limited by the unmodified material remaining in the film after the initial exposure period.

2:40pm **PS1-WeA3 Deciding Factors for Line-Edge-Roughness (LER) Formation and Plasma-Resistance of ArF Photoresist during Plasma Etching Processes**, ***T. Uesugi**, K. Koyama, B. Jinnai,* Tohoku University, Japan, *S. Maeda, K. Kato, A. Yasuda, H. Momose,* Mitsubishi Rayon Co., Ltd, Japan, *S. Samukawa*, Tohoku University, Japan

ArF excimer laser (193nm) lithography is used in the fabrication of sub-100-nm devices. However, during plasma etching processes, activated species radiated from plasma, such as ions, radicals, and photons, degrade ArF photoresist, resulting in low etching resistance and the formation of line-edge roughness (LER). To solve these issues, it is important to understand the interaction of plasma and ArF photoresist and to clarify deciding factors for the plasma resistance and the formation of LER in ArF photoresist. For this purpose, using our developed neutral beam process, effects of the activated species from plasma are divided into physical bombardment (by ions), chemical reactions (by radicals), and UV radiation. UV radiation drastically increased the etching rates of ArF photoresist films, and, in contrast, chemical reactions enhanced the formation of surface roughness in ArF photoresist. FTIR analysis shows that UV radiation preferentially dissociates C-H bonds in ArF photoresist, rather than C=O bonds, because of these bond dissociation energies; E(C-H, 4.25eV) < E(C=O, 7.71eV). This indicates that the etching rates of ArF photoresist are determined by UV radiation, because UV radiation can break C-H bonds, which are a majority of structures in ArF photoresist. On the other hand, according to the FTIR analysis, c hemical species, such as radicals and ions, are likely to react with C=O bonds, especially C=O bonds in lactone groups of ArF photoresist due to the structural and electronic effects of lactone groups. As a result, the etching rates of ArF photoresist can microscopically vary in different bond structures, leading in the enhancement of surface roughness in ArF photoresist. To reduce the chemical reactivity and the surface roughness, radical trap additives were injected into ArF photoresist. Radical trap additives, which can reduce surface roughness by 30%, are very effective to suppress the roughness formation in ArF photoresist.

3:00pm **PS1-WeA4 Smoothening of 193 Immersion Resist by 172 nm VUV Exposure**, ***E. Kunnen**, A. Vaglio Pret,* IMEC, Belgium, *O. Luere,* CNRS-LTM, France, *L. Azarnouche,* STMicroelectronics, France, *E. Pargon,* CNRS-LTM, France, *P. Foubert, R. Gronheid, D. Shamiryan, M.R. Baklanov, W. Boullart*, IMEC, Belgium

At today's date 193 immersion lithography is used in semiconductor industry to print lines of less than 40nm half pitch, continuing the scaling. One of the challenges is to reduce line edge variations, or Line Width Roughness (LWR). It has already been pointed out earlier that LWR can be significantly reduced during the subsequent dry etch step. One of the important components acting on LWR during the dry etch is the VUV light emitted from the plasma, however, the exact mechanism is not yet revealed.

The photoresist pattern profile and its chemical modifications are studied as a function of VUV dose. A 172 nm Xe_2* excimer 30mW/cm^2 light source is used to expose patterned and blanket (resist & organic BARC) wafers, exposing them from 2 to 256 seconds under nitrogen ambient and controlling the temperature within 2°C. SEM-CD top-down image analysis gives us spatial and information in both spatial and frequency domain through Critical dimension (CD), CD-Uniformity, LWR and Power Spectr al Density (PSD). Three dimensional information is recorded by CD AFM measurements. The thickness, refractive index and extinction coefficient are deduced from spectral ellipsometric (SE) measurements. Mass measurements provide density. Fourier Transformed Infrared Spectroscopy

* Coburn & Winters Student Award Finalist

(FTIR) analyses provide information on the molecular bonds. Finally, chemical analysis will be performed by elastic recoil detection (ERD) and Time of flight secondary ion mass spectrometry (TOFSIMS).

Significant changes in CD and LWR are observed up to 12s (360 mJ/cm^2) of VUV exposure time corresponding to a dose of about 1 photon per atom. For higher exposures the integrity of the lines deteriorates compromising the accuracy in the SEM-CD analyses. Initially, CD and LWR decreases while the correlation length increases. PSD analysis shows that the reduction is attributed to a decrease in the high frequency roughness region. For longer exposure, a CD increase is observed and finally low frequency roughness increases, the total LWR. The CD evaluation indicates a resist reflow that is driven by surface tension towards a more rounded shape. Mass and thickness measurements over the whole exposure range show a decrease that goes linearly with the logarithm of the exposure time, while density remains about constant. FTIR indicate a correlation of the observed changes with the removal of the lactone bonds at 1800 cm-1.

In conclusion the dose range at which VUV impacts LWR is measured to be around 1 photon/atom. Initially a CD and LWR decrease is observed while for larger doses the trend is the opposite. Change of mass and thickness follows a first order kinetic equation, which is quite typical for simple desorption processes.

4:00pm **PS1-WeA7 Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Surface Roughening: the Dependence on Polymer Structure**,
***T.-Y. Chung**, D.B. Graves,* University of California, Berkeley*, F. Weilnboeck, G.S. Oehrlein,* University of Maryland*, E.A. Hudson,* Lam Research Corporation*, M. Li*, The Dow Chemical Company

Previous vacuum beam studies showed that methacrylate-based 193 nm photoresist (PR) will roughen due to the synergistic effects of ion bombardment, vacuum ultraviolet (VUV) photon and substrate heating [1]. The surface roughness and surface morphology is similar to that after inductively coupled argon plasma exposure under similar ion and VUV fluences and energies [2]. However, 193 nm PR is a heteropolymer, with three separate side-groups that could be photolyzed due to the plasma-generated VUV, and this could complicate analysis of roughening mechanisms. We therefore examined several associated homopolymers to better understand the role of the side groups in roughening under plasma exposure. We chose two homopolymers: 2-methyl-2-adamantyl methacrylate (MAMA, leaving group) and R-functionalized adamantly methacrylate (RAMA, polar group). At a substrate temperature of 65˚C, MAMA undergoes considerable loss of material under VUV-only exposure. In addition to the loss of CH2/CH3, C=O and C-O-C bonds in the polymer bulk observed by transmission Fourier transform infrared (FTIR) spectroscopy, mass spectroscopy analysis shows that the adamantane leaving group is lost from the film. In contrast, RAMA is relative insensitive to VUV irradiation. After simultaneous ion/VUV exposure at a substrate temperature of 65˚C, MAMA shows very high surface roughness while RAMA shows little surface roughening. The surface of MAMA is also significantly rougher than that of 193 nm PR processed under the same condition. It therefore appears that the leaving group in 193 nm PR, designed to cleave in the presence of photoacid during lithographic exposure and post-exposure bake, is the primary cause of 193 nm PR roughening, when combined with energetic ion bombardment, VUV irradiation and elevated heating.

[1] D. Nest, T.-Y. Chung, D. B. Graves, S. Engelmann, R. L. Bruce, F. Weilnboeck, G. S. Oehrlein, D. Y. Wang, C. Andes, and E. A. Hudson, Plasma Process. Polym. 6 (2009) 649.

[2] M. J. Titus, D. G. Nest, T.-Y. Chung, and D. B. Graves, J. Phys. D, Appl. Phys. 42 (2009) 245205.

4:20pm **PS1-WeA8 Polymer Surface Modification: Vibrational Sum Frequency Generation Study for Plasma Etching**,
***K. Ishikawa**, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

A comprehensive understanding of interaction between plasmas and nano-materials is essential for advanced plasma processing technology. By means of plasma-beams apparatus, complicated processes are expectedly convolved individual contributions such as ion, radical, and photons. The vibrational sum-frequency-generation (SFG) is a beneficial tool for addressing best sensitivity at surface and interface, breaking their centro-symmetry[1]. In this study, we have investigated polymer surfaces exposed to the plasma-beams by using SFG.

Samples used were spin-on methyl-siloxane polymer, which is able to used as low-dielectric-constants (Low-k) film for interconnects. Hydrophobic property exhibits since methyl end group, -CH_3, is terminated at end on siloxane.

Plasma beams, which directly extracted from a argon plasma by acceleration between 100 and 400 eV, were irradiated.

The SFG spectroscopy setup consists of a 1064 nm Nd:YAG laser, and optical systems, which create both visible (532 nm) and tunable infrared (1000-4000 cm^{-1}) radiations (Ekspla). The SFG spectra taken were decomposed into individually spectral features by fitting spectra calculated to that measured. Intensity of SFG signal emitted from the surface is phenomenogically expressed as the summation of non-resonant susceptibility and damped Lorentian oscillators, which are characterized by phases, strength, resonant, and damping wavenumber.[2]

Before plasma exposure, peaks at ~2930 and ~2970 cm^{-1} are arisen from C-H stretch of Si-CH_3. This strength coincides with that for a peak at around 1275 cm^{-1} in infrared spectra. After plasma exposure, surface methyl group is disappeared. At the present, it was interpreted that at early stage under ion irradiation, hydrogen is released from the end-on methyl group to create surface radicals, namely rupture of chemical bonds to methyl group is essential for elimination from end-groups on the surface.[3] Further detailed considerations should be conducted.

The surface modifications of plasmas have been studied by using the plasma-beam apparatus and the SFG spectroscopy. The end-groups of the polymer surface were changed only physical ion bombardments. To understanding surface chemical reactions and physical properties, nano- and atom- scaled views of not only bulk materials but also surface end-groups are informative.

Acknowledgments

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References

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[2] A. G. Lambert et al, Appl. Spectrosc. Rev. 40, 103 (2005).

[3] K. Ishikawa, *et al*., J. Appl. Phys. 99, 083305 (2006).

4:40pm **PS1-WeA9 Plasma-induced Mechanical Degradation of Silicon Microcantilever**,
***C.H. Huang**, M. Tomura, Y. Yoshida, T. Ono,* Tohoku University, Japan*, S. Yamasaki,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*, S. Samukawa*, Tohoku University, Japan

Miniaturization of microcantilever realized increasing resonant frequency and achieving high resolution in image sensing devices such as scanning probe microscopy. Thin film deposition and etching are widely used in micro fabrication process. Therefore, it is indispensible to use plasma process. However, the plasma process usually generates defects in the micro structure due to the high-energy ion bombardment, charge build-up and UV photon radiation from the plasma, which might degrade the mechanical characteristics of the micro elements, such as microcantilever, and result in MEMS malfunction.

In this study, a Si microcantilever was adopted to investigate the influence of plasma irradiation to mechanical characteristic. The Si microcantilever was fabricated with silicon on insulator wafer. After the fabrication, the microcantilevers were irradiated by inductively coupled plasma and neutral beam (NB) with argon gas at room temperature. The influences of the plasma and NB irradiations on Si microcantilevers were evaluated with Q factor and resonant frequency (f) using laser Doppler vibrometer before and after irradiation. After plasma irradiation, Q factor ratio [Q factor after irradiation/Q factor before irradiation] and f ratio [f factor after irradiation/f factor before irradiation] drastically decreased. The Q factor ratio didn't depend on the irradiation time and the f ratio decreased as the plasma irradiation time increased. On the other hand, the Q factor ratio and f ratio only slightly decreased after Ar NB irradiation, which indicates that NB process have great potential for MEMS application. To understand the degradation mechanism of Si microcantilever, defect (E' center) density on microcantilever surface was measured by electron spin resonance. The defect density increased when plasma irradiation time increased. The Young's modulus (E) of microcantilever calculated from f suddenly decreased and became plateau when E' center was over a threshold defect density. The Q ratio decreased when the microcantilever thickness decreased. It is because the ratio of defect depth to microcantilever thickness being higher. Given these results, plasma irradiation degrades the E resulting in the variation of the f. D egradation of Q factor is determined by the ratio of defect depth to microcantilever thickness.

5:00pm **PS1-WeA10 Gas-phase Diagnostics for Understanding Plasma Processing to Tailor the Surfaces of Inorganic Thin Films and Nanoparticles**,
K.J. Trevino, S.M. Thagard, J.C. Shearer, J.M. Stillahn, ***E.R. Fisher***, Colorado State University

Plasma-enhanced chemical vapor deposition (PECVD), plasma etching, and plasma modification of surfaces are emerging as important tools in the development of biomaterials, hard coatings and other diverse applications. Recently, we have explored the use of both low-pressure rf plasmas as well

as atmospheric plasmas to specifically tailor the surface properties of a variety of inorganic materials with a range of morphologies from flat substrates to membranes and nanoparticle systems. Despite the broad range of applicability of plasma processing for producing materials with specific surface properties (e.g. hydrophilicity, chemical functionality, etc.), many mechanistic details remain unknown. Understanding the contributions of gas-phase species is critical to understanding the chemistry that leads to specific surface modifications. In addition, the surface interactions of gas-phase plasma species provide critical molecular level information about plasma processing, especially at interfaces. In addition, power dissipation and energetics are also important for elucidation of mechanistic details in plasmas. The imaging of radicals interacting with surfaces (IRIS) technique uses laser-induced fluorescence (LIF) to provide spatially-resolved images of plasma species. Furthermore, IRIS provides direct information on the energetics of plasma-generated radicals as well as for species scattering off of surfaces. Combined with quantitative optical emission spectroscopy (OES) data, we have measured the internal and translational temperatures for a range of species in a variety of plasma environments. This work concentrates on OH radicals in H_2O plasmas used to create hydrophilic metal oxide surfaces, CH radicals in plasma polymerization systems for nanocomposite materials, and, SO_2 and CF_x species in dielectric etching systems. For many of these molecules, vibrational temperatures are significantly higher than rotational temperatures and the partitioning of energy is correlated to surface reactivity. Comparison between atmospheric and low temperature plasmas as well as flat vs. nanostructured substrates will be made. Preliminary results from computational models of our plasma systems will also be presented. The gas-phase data are complemented by a range of surface and materials analysis data that reveal a more detailed picture of the overall plasma process in each system.

5:20pm **PS1-WeA11 Wet SiO_2 Etch Rate Enhancement Due To Surface Fluorination By A Remote O_2/CF_4 Plasma**, ***D.L. Gilbert***, Mattson Technology Singapore PTE LTD

High Dose Implantation (HDI) for source/drain (S/D) is one of the critical steps for transistor formation. It becomes more complicated due to S/D junctions are designed to be shallower at proportional scaling down of the entire transistor. The photo resist (PR) mask is exposed to increasing number of implant species, higher dosages and energy levels. The top layer of the PR transforms to hard and cross-linked crust. Meanwhile, the sidewall of the PR mask collects a lot of spattered substrate (inorganic) materials. As a consequence, HDI photo resist strip (HDIS) is increasingly difficult to get residue free with controlled material loss and growth as required at lower node. One of widely used HDIS process solutions is remote O_2/CF_4 plasma followed by a wet chemical clean, such as dilute HF and/or SC1 solutions. However, these strip / clean processes also attack the underlying SiO2 films. It is critical to control such SiO2 loss for future IC production, as device sizes shrink. Therefore, a delicate balance is to be discovered between effectively cleaning the wafer surface and etching into the SiO2 substrate. This paper discusses the significant synergy between the O_2/CF_4 processes and subsequent wet clean. It has been observed that the overall oxide removal through combined O_2/CF_4 dry clean and wet chemical clean is significantly higher than the sum of the independent oxide loss through dry clean and wet clean. The effect on CF_4 concentration in the plasma, O_2/CF_4 processing time, and temperature on the wet etch rate enhancement are explored. In an effort to reduce the etch rate enhancement, several post O_2/CF_4 processes such as a O_2 only plasma, a forming gas plasma, and a simple water rinse are employed. Results show that the oxide loss enhancement is due to the presence of a highly fluorinated surface post O_2/CF_4 dry clean. This fluorinated oxide surface readily dissolves in wet etch chemistries. Furthermore, once desorbed from the wafer surface, the fluorine may increase the local concentration of species responsible for etching oxide films.

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