

Wednesday Morning, October 30, 2013

Plasma Science and Technology

Room: 104 C - Session PS-WeM

Fundamentals of Plasma Surface Interactions

Moderator: S.A. Vitale, MIT Lincoln Laboratory

8:00am **PS-WeM1 Examination of Atomistic Etching Control of SiO₂-Si-SiO₂ Multi-Layers Stacks Using Cyclic Ar/C₄F₈ Plasma**, *D. Metzler, G.S. Oehrlein*, University of Maryland, College Park, *S.U. Engelmann, R.L. Bruce, E.A. Joseph*, IBM T.J. Watson Research Center

There is great interest in establishing directional etching methods capable of atomic scale resolution for fabrication of highly scaled electronic devices. We report on controlled etching of sub-nm thick layers of silicon and SiO₂ using cyclic Ar/C₄F₈ plasma. The work was performed in an inductively coupled plasma reactor. Use of SiO₂-Si-SiO₂ multi-layers on a Si substrate enables precise examination of selectivity, etch stop, and modification using *in situ* ellipsometry. Controlled etching is based on deposition of a thin (<1 nm) reactive fluorocarbon (FC) layer on SiO₂-Si-SiO₂ layers using pulsed C₄F₈ flow. Subsequent Ar⁺ ion bombardment removes the FC layer along with SiO₂ from the surface. Ar⁺ ion bombardment energies were selected so that once the FC layer had been removed, etching ceased. If ion energies are too high, significant SiO₂ etching takes place and a self-limited process cannot be achieved. The impact of deposited FC layer thickness on SiO₂ etching and etch selectivity relative to Si is examined and quantified. Additionally, x-ray photoemission spectroscopy (XPS) studies are used to investigate surface chemistry at various stages of the cyclic surface etching and will be reported. We found that chamber condition, especially inadvertent fluorocarbon deposition on the chamber walls concurrent with ultra-thin FC layer deposition on the substrate surface, can have a strong impact on the etch characteristics. The authors gratefully acknowledge financial support from National Science Foundation award CBET-1134273.

8:20am **PS-WeM2 Plasma Induced Surface Roughness of ArF Photoresist Examined by Plasma-Beam Processes**, *T. Takeuchi, Y. Zhang, K. Ishikawa, M. Sekine*, Nagoya University, Japan, *Y. Setsuhara*, Osaka University, Japan, *K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan

We report an observed relationship between chemical modifications and physical morphological roughness on a photoresist for ArF excimer laser photolithography in plasma beam irradiation. In fluorocarbon plasma, at the very beginning period, three stages of characteristics of chemical changes occurred upon surface roughening or wrinkling of the photoresist; (1) a rapid reduction of C=O bonds, (2) gradual formation of a fluorocarbon layer, and graphitic (sp²-C) or amorphous (sp³-C) carbon layer; (3) as elapsed incubation phase, i.e. lag, where reached a steady-state of chemical changes for fluorocarbon ion irradiation on the surface; finally morphological changes initiated. Those processes evolved within dose of $6 \times 10^{15} \text{ cm}^{-2}$ for ion energy of a few hundred eV [1].

Furthermore, in hydrogen plasma, especially in annealing at approximately 160°C, the photoresist surface was corrugated with size of the order of microns as similar as the report about mechanically buckling [2]. Subsequently the roughen surface was treated by the plasma beam irradiation, the roughness was developed with a size of the order of nanometers as same as the previous report [1]. Therefore we are revisiting the roughening process on the plasma process [3], and we will discuss on the roughening phenomena on the photoresist during plasma processes.

References [1] T. Takeuchi *et al.*, J. Phys. D **46**, 102001 (2013). [2] H. Jiang *et al.*, PNAS **104**, 15607 (2007). [3] R. Bruce *et al.* J. Appl. Phys. **107**, 084310 (2010).

8:40am **PS-WeM3 Sidewall Polymer Deposition for Achieving Near 1:1 x:y Critical Dimension Shrinkage**, *N.A. Fox-Lyon, D. Metzler, A.J. Knoll*, University of Maryland, College Park, *T. Liu, D. Farber*, Texas Instruments, *G.S. Oehrlein*, University of Maryland, College Park

New methods for shrinking lateral features are required to extend current generation photoresist patterning to smaller structures for devices. One approach for this is deposition onto sidewalls of patterned features using plasma-etch equipment. Current issues with this method are creating significant and uniform (x,y dimensions) pattern shrinkage and minimizing roughness and deformation of patterned features. In this work, we explored shrinking circular/elliptical holes and lines in 248 nm photoresist and 193 nm films using plasma-enhanced deposition in combination with etching. Both hydrocarbon and fluorocarbon plasma mixtures with inert/reactive carrier gases were evaluated for deposition. Plasma parameters for shrinkage were chemistry (e.g., ratio of deposition gas to carrier gas flow),

pressure, applied power, ion energy (by substrate biasing), and deposition time. Real-time *in situ* ellipsometry and x-ray photoelectron spectroscopy of deposited films and scanning electron microscopy of patterns were carried out for characterization. We report on the plasma parametric dependencies of top-down and sidewall deposition rates, along with optical density and chemical composition of the films. Cyclical deposition/etching and pulsed plasmas were also explored for achieving shrink and minimizing sidewall roughness. Statistical analysis of x:y shrink, top-down deposition to sidewall deposition, and sidewall/surface roughening was investigated. We find strong dependencies on sidewall shrink on feature size and aspect ratios. As feature sizes get below 50 nm, minimizing feature roughness/occlusion becomes more difficult for the plasma parameters explored. Achieving significant 1:1 x:y sidewall shrink requires fine control of the plasma parameters that can change during deposition. By fine-tuning plasma parameters we have achieved 10's of nm of 1:1 x:y sidewall shrink of circular/elliptical patterned photoresist features.

9:00am **PS-WeM4 Plasma Energy Partitioning and Influences on Surface Reactivity**, *J.M. Blechle, M.F. Cuddy, E.R. Fisher*, Colorado State University

The partitioning of energy within plasma systems is of vital importance to plasma chemistry as it provides insight into reactivity via possible formation and decomposition mechanisms as well as its significant contribution to surface reactivity. Here, such investigations are used to determine the internal and kinetic energies of species within a variety of inductively coupled plasma systems. To obtain this information, optical emission spectroscopy (OES), broadband absorption spectroscopy (BAS), and the imaging of radicals interacting with surfaces (IRIS) technique were utilized to determine species energetics (vibrational, rotational, and translational temperatures). Although comparisons will be made between internal energies of SiF in SiF₄ plasmas and CF in variety of fluorocarbon plasmas, a primary focus will be placed on nitric oxide plasma systems and the associated energies of NO gas species. These data are also correlated to species surface reactivity data, and are used to demonstrate the relationship between internal temperatures and observed surface scatter coefficients (S), which is directly related to surface reactivity (R). One such comparison will be on the strong correlations measured between the vibrational temperatures (Θ_v) of NO and S(NO) as a function of applied plasma power. Such observations allow for unique insight into these plasma systems and the integral role energy partitioning plays in the assessment and understanding of complex plasma chemistry.

9:20am **PS-WeM5 H₂/D₂/Ar Plasmas Interacting with Carbon-based Films: Plasma Distribution Functions, Etching and Applications**, *N.A. Fox-Lyon**, *A.J. Knoll*, University of Maryland, College Park, *J. Franek*, West Virginia University, *V. Demidov*, Wright-Patterson Air Force Base, *M. Koepke*, West Virginia University, *G.S. Oehrlein*, University of Maryland, College Park

Prediction and control of plasma distribution functions in low temperature plasmas are important for control of plasma-materials interactions. Reactive impurity additions to inert plasmas are important due to their large effects on both plasma properties and role in plasma-surface interactions. H₂ and/or D₂ added to Ar is an increasingly large topic of interest. The addition of small amounts of H₂/D₂ to Ar cause a change from physical to chemical sputtering of etching surfaces. Sode *et al.* have shown that small additions of H₂ to Ar cause unpredicted distributions of ion composition and a large loss in plasma density [1]. We investigate the effect that addition of small amounts of H₂/D₂ has on the ion compositions and energy distributions, along with effects on the plasma electrical properties and neutral and metastable species. D₂ addition to Ar plasma causes a faster transition to predominant ArD⁺ ions than H₂ addition causes transition to predominantly ArH⁺ ions. We also report on the effect H₂/D₂ added to Ar plasma has on the Ar metastable concentration. We find that, like the effect on plasma density, the metastable concentration decreases rapidly with the introduction of H₂ impurities. We find measureable differences for these effects when using D₂ impurity instead of H₂ impurity. The effect of these changes to plasma properties by H₂/D₂ impurity addition is also reflected in the plasma material interactions with hydrocarbon films. While ion mass falls gradually with addition, etch rate and modification change drastically. Direct plasma and neutral-based etching experiments were performed for different chemistries to separate the effects of ion composition/mass and reactive neutrals generated in the plasma. The authors gratefully acknowledge financial support from US Department of Energy (DE-SC0001939).

* Coburn & Winters Student Award Finalist

9:40am **PS-WeM6 Molecular Dynamics Simulation for Hydrogen Plasma Processing of Graphene**, A. Davydova*, E. Despiau-Pujo, G. Cunge, Cnrs/ujf/ Cea - Ltm, France, D.B. Graves, University of California, Berkeley, L. Magaud, L. Delfour, CNRS/UJF, Institut Néel, France

Graphene is a two-dimensional material with unique physical, chemical and mechanical properties, promising for novel applications in industrial scale. The successful development of graphene-based thin film technologies relies on the capability to grow and integrate this material into sophisticated devices, but the nm-scale control of graphene processing challenges current technology, especially in plasma treatment.

The main issue associated with plasma/graphene processes is the few-to mono-atomic thickness of the material: graphene is easily damaged upon exposure to reactive plasma. This precludes the use of conventional plasma technologies to clean, dope and pattern graphene layers in a controlled way as is done for other materials in the microelectronic industry. Pulsed inductively coupled plasmas (ICPs) could in principle alleviate this issue by reducing ion bombardment energy while retaining active radicals. Hydrogen plasma has been shown to be promising for graphene treatment with minimal damage, but little is known of the fundamental mechanisms.

In this work, we applied classical molecular dynamics (MD) simulations of H₂ plasma / graphene interaction to assist the development of two important processes: graphene surface cleaning (selective removal of polymeric PMMA residues from its surface) and graphene nanoribbon (GNR) patterning with well controlled edges. Using MD we investigate the impact of the graphene temperature and incident H species energy on nanoribbon modification. We found that on the ribbon basal plane, H species experienced a repulsive force due to delocalized π -electrons, which prevents them from chemisorption if their energy is below ~ 0.6 eV. By contrast, there is no barrier for H chemisorption on GNR edges and the graphene border can be rapidly hydrogenated by H radicals without damaging the basal plane. MD simulations further suggest that lateral etching will not occur unless the graphene temperature is raised above ~ 600 K and that etching probability slows above about 800K. This result is in good agreement with experiments. We also show that exposure of graphene to energetic H above a threshold of ~ 12 eV leads to H penetration through graphene. Severe damage of the graphene basal plane (i.e. C-C bond breaking) is observed at incident H energies higher than ~ 15 eV. This suggests that ions and fast neutrals from pulsed ICPs, which impact surfaces at ~ 1 -10 eV, may be well suited for graphene cleaning and GNR trimming. This result has now been confirmed experimentally. XPS, AFM, Raman and electrical measurements show that pulsed H₂ plasmas clean PMMA residues from graphene surface with almost no damage after annealing.

10:40am **PS-WeM9 Beam Studies of Plasma Etching Reactions**, K. Karahashi, S. Hamaguchi, Osaka University, Japan **INVITED**

For the development of highly integrated semiconductor devices, more precise control of etching processes is required for further progress. For this purpose, it is desirable to have full understanding of surface reaction mechanisms associated with the etching processes. However, in general, it is difficult to analyze such reactions in detail for plasma etching processes because a large number of reactions take place simultaneously. One way to tackle this challenge is use a beam system to examine specific beam-surface interactions that are likely to take place in actual plasma etching processes. Pioneering work by Coburn *et al.* [1] using beam experiments clearly showed that silicon etching reactions on fluorinated surfaces are enhanced by energetic inert ion bombardment. Many such studies have provided useful qualitative information on silicon etching by plasmas based on, for example, halogen gases. As new advanced semiconductor devices have been proposed, the variety of materials that require highly controlled etching and that of gases that are used for the reactive ion etching (RIE) processes have increased significantly. Therefore we believe that needs for such beam studies are higher than ever. Based on an earlier beam system [2], we have recently advanced our techniques to examine interactions of reactive ions and free radicals with material surfaces, using a multi-beam system. With this system, we have obtained detailed information on reactive etching and physical sputtering processes on various materials such as silicon, silicon oxide, silicon nitride, and metals including ferromagnetic materials. The multi-beam system is a mass-selected ion beam injector combined with supersonic molecular beam and effusive molecular beam sources. When a sample is irradiated with any combination of these beams, it exhibits a specific surface reaction that would take place in an actual plasma. Its surface analyses include *in-situ* chemical analyses by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy and angular and time-resolved measurements of desorbing molecules by a rotatable QMS. In the presentation, a detailed account will be given of how such beam

experiments unveil surface reaction mechanisms for RIE processes, based on examples of four recent studies on selective etching processes of Si-based materials and metals. [1] J. W. Coburn, H. F. Winters, and T. J. Chuang: J. Appl. Phys. **48**(1997) 3532. [2] K. Karahashiet *al.*: J. Vac. Sci. Technol. A **22**(2004) 1166

11:20am **PS-WeM11 Surface Cleaning for Enhanced Adhesion to Packaging Surfaces: Plasma and Free Radical Chemistries**, S. Gaddam, H. Kasi, J. Kelber, University of North Texas

In microelectronics device packaging, the removal of adventitious carbon and other contaminants, and the formation of a hydrophilic surface, are key steps to ensure adequate bonding to epoxy. This surface cleaning is commonly accomplished by oxygen plasma treatment, but the effects of such treatment on contaminant removal, surface composition and surface hydrophilicity are not well-understood. In-situ x-ray photoelectron spectroscopy (XPS) indicates that He, O₂ and NH₃ capacitively-coupled plasmas are equally effective at removing adventitious carbon from silicon nitride (SiN_x) and Si oxynitride (SiO_xN_y) surfaces. O₂ or He plasma treatment, however, results in initial oxidation of SiN_x or SiO_xN_y surfaces, and eventual formation of a SiO₂-like overlayer. In contrast, exposure of either surface to thermal atomic O yields carbon removal, but only surface oxidation of SiN_x, and no further change in SiO_xN_y surface composition. The data demonstrate that silica overlayer growth involves reaction of background O₂ or H₂O with reactive sites induced by ions or vacuum ultraviolet photons present in the plasma. In contrast, the exposure to NH₃ plasma results in negligible surface oxidation of the SiN_x or SiO_xN_y surfaces, but with effective removal of the adventitious carbon. There is no formation of a SiO₂ overlayer even at higher exposure times. This indicates that the presence of H passivates or reduces reactive sites for SiO₂ formation at the Si_xN or SiO_xN_y surfaces. Ex-situ contact angle measurements show that SiN_x and SiO_xN_y surfaces exposed to oxygen plasma are initially more hydrophilic than surfaces exposed to NH₃ plasma, indicating that the O₂ plasma-induced SiO₂ overlayer is highly reactive towards ambient. At longer ambient exposures ($> \sim 10$ hours), however, surfaces treated by either method exhibit similar steady state contact angles, correlated with rapid uptake of adventitious C, as determined by XPS. These data demonstrate that O₂ or even He plasma cleaning of SiN_x or SiO_xN_y surfaces results in unintended SiO₂ overlayer formation and that the use of NH₃ plasma can clean the substrates efficiently without the SiO₂ formation. The data also demonstrate that the hydrophilicity of such surfaces decreases rapidly upon ambient exposure, suggesting the potential advantage of in-situ surface passivation following plasma cleaning.

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