

Thursday Morning, November 12, 2009

Plasma Science and Technology

Room: A1 - Session PS1-ThM

Applications of Plasma-Surface Interactions

Moderator: L. Stafford, Université de Montréal, Canada

8:00am **PS1-ThM1 Coupled Ion, Photon and Electron Synergies in Plasma-Surface Interactions for Organic Materials**, *D.B. Graves*, University of California at Berkeley

Recent experimental and simulation studies have revealed that plasma-organic surface chemistry can be strongly affected by synergistic interactions among ions, vacuum ultraviolet (VUV) photons and electrons at surfaces. In this talk, I summarize our recent studies of these synergies, focusing on various polymer and SiCOH low-k dielectric materials. When plasma and vacuum beam measurements, coupled with molecular dynamics (MD) simulations, are compared for various materials and various exposure conditions, certain patterns emerge. MD shows that (~ 100 eV) ion effects are restricted to several nm near the surface, but that their effects can depend strongly on the type of polymer and other species present. The synergistic effects of plasma-generated ions, photons and electrons can be understood in terms of a competition between bond-breaking scissioning reactions and bond-forming cross-linking and other reactions. The complexity of the results is due in part to the fact that these species have different depths of penetration, and that their bond breaking and bond forming reactions depend on the structure of the material. However, even greater complexity results from the fluence- or dose-dependent nature of electrons and ions: low dose result in scissioning and higher doses result in cross-linking. The effects of simultaneous exposure depend on both position relative to the surface and time. I illustrate these ideas with examples taken from PMMA-based 193 nm photoresists; poly-alpha methyl styrene (PaMS) and poly-four methyl styrene (P4MS); and ultra low k, nanoporous SiCOH. MD simulations and models of VUV photon penetration into polymers are used to interpret both plasma and vacuum beam experimental results.

8:20am **PS1-ThM2 Control of Photoresist Erosion in SiO₂ Plasma Etching in DC Augmented CCP Tools**, *M. Wang*, Iowa State University, *M.J. Kushner*, University of Michigan

Polymer photoresists are commonly used for pattern transferring in plasma etching of sub-0.1 micron features in microelectronics fabrication. Degradation and erosion of the photoresist (PR) is a major issue in controlling feature profiles, especially for high aspect ratio (HAR) features where etch times are long. For example, during fluorine based plasma etching of SiO₂, erosion of the photoresist leads to bowing of the top of the profile as the etch proceeds. Multilayer masking is one approach to minimize these effects. By depositing a hard mask layer under the PR, the pattern is transferred to the hard mask layer before the PR is eroded away. Another promising strategy is to deposit a hard mask layer onto the PR surface during the process. This can be achieved in-situ by low energy ion bombardment of the PR surface to both promote cross-linking and produce dangling bonds, coincident to there being a flux of Si radicals. The resulting Si-C bonding provides a hard-mask like surface. Another is to promote fluorocarbon deposition on the PR mask to slow its erosion. These opportunities may be afforded by dc-augmented capacitively coupled plasmas (CCPs) in which the silicon covered dc electrode is sputtered. In this talk, we discuss scaling laws for profile and PR control derived from a computational investigation of a dc augmented single/dual frequency CCP reactor to generate an Ar/C₄F₈/O₂ plasma and fluxes of Si radicals by sputtering the dc electrode. Fluxes (energy and angle resolved) of ions, radicals and electrons are obtained from the Hybrid Plasma Equipment Model (HPEM) as a function of dc voltages, rf frequencies and rf bias powers. Profiles of features are then simulated by the Monte Carlo Feature Profile Model (MCFPM). Both multilayer mask and Si deposition strategies will be discussed. Etching selectivity between SiO₂ and mask material and feature profiles will be discussed as functions of Si fluxes, initial patterns and thickness of the photoresist.

*Work supported by Tokyo Electron Ltd., and the Semiconductor Research Corp.

8:40am **PS1-ThM3 Ultimate Top-down Processes for Future Nanoscale Devices - Novel Neutral Beam Process and Control of Atomic Layer Chemical Reaction**, *S. Samukawa*, Tohoku University, Japan **INVITED**

For the past 30 years, plasma etching technology has led in the efforts to shrink the pattern size of ultralarge-scale integrated (ULSI) devices. However, inherent problems in the plasma etching, such as charge build-up

and UV photon radiation, limit the etching performance for nanoscale devices. To overcome these problems and fabricate sub-10nm devices in practice, neutral-beam process has been proposed. In this paper, I introduce the ultimate etching processes using neutral-beam sources and discuss the fusion of top-down and bottom-up processing for future nanoscale devices. Neutral beams can perform atomically damage-free etching and surface modification of inorganic and organic materials. Namely, the neutral beam process can precisely control the atomic layer chemical reaction and defect generation. This technique is a promising candidate for the practical fabrication technology for future nanoscale devices.

9:20am **PS1-ThM5 Accurate Control of Ion Bombardment in an Expanding Thermal Plasmas**, *P. Kudlacek*, *R.F. Rumphorst*, *A. Illiberi*, *M.C.M. van de Sanden*, Technical University Eindhoven, The Netherlands

Remote plasmas are extensively used in industry for both etching and deposition of materials. As ion bombardment has been found to be crucial for controlling deposited material properties or enhancing etch rate and anisotropy during ion induced etching, an additional bias voltage is often applied to the substrate to control the energy of the bombarding ions and/or enlarge their flux onto the substrate. Recently, a pulsed bias scheme became subject of increased interest as a promising technique to reach narrow, almost mono-energetic ion energy distribution (IED) when dielectric substrates are being processed, especially considering that the conventionally used radio frequency bias inherently leads to a bimodal IED. Moreover it offers an ultimate control of the ion flux onto the substrate by varying the duty cycle.

Experiments were run in a remote expanding thermal plasma (ETP) reactor, in Ar and Ar/H₂ gas mixture compositions. The substrate holder was negatively biased (up to -100V) by means of a home designed pulsed power supply operating with a frequency up to 200 kHz and a variable duty cycle. Ion energy distributions have been measured by means of a planar gridded retarding field energy analyzer.

Two pulsed biasing approaches will be presented (asymmetric rectangular pulses and modulated pulses with a linear voltage slope during the pulse) and their applicability is discussed on the basis of an intrinsic capacitance of the processed substrate-layer system. The substrate voltage and current waveforms were measured and mutual relations with the obtained ion energy distributions will be shown for both aforementioned cases. To demonstrate the IED control achieved, the effective carrier lifetime of n-type c-Si wafers, passivated by an a-Si:H thin film, as a function of the flux and energy of bombarding argon ions was determined. The ion energy and ion flux was independently varied and threshold ion bombardment characteristics leading to degradation of the effective lifetime will be presented.

9:40am **PS1-ThM6 Plasma Induced Modification of an Organic Photoconductor in an Electrophotographic System**, *K. Nauka*, *S. Chang*, *H.-T. Ng*, Hewlett-Packard Company

The goal of this study was to elucidate structural and compositional modifications of an organic photoconductor after an extensive exposure to plasma discharge by a charging element within an electrophotographic system. An organic photoconductor, commonly found in a variety of applications ranging from simple copiers to advanced high-speed digital presses, is the key element of the modern electrophotographic printing system. It facilitates formation of the latent image resulting from the area-selective light discharge of uniformly distributed charges deposited on its surface by the plasma. Its undesirable modifications may adversely impact the print quality.

Modifications of the photoconductor's surface layer were investigated with the help of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR) and X-ray Photoelectron Spectroscopy (XPS). The experimental set-up was designed to simulate interactions between the plasma discharge and photoconductor occurring in a typical electrophotographic printing environment. Experiments were performed over an extended period of time corresponding to printing multiple pages. UV radiation and energetic particle bombardment originating from the plasma are the two major processes responsible for the photoconductor modifications. Therefore, further elucidation of the photoconductor modification phenomenon was obtained by employing the UV-only and the particle bombardment-only experimental conditions.

A long time exposure of the photoconductor to energetic neutral and charged species, and UV photons caused massive oxidation, substantial chemical bond breakage, and reformation of bonding configuration within a thin layer below the surface. This layer can be divided into two regions corresponding to the aforementioned photoconductor modification processes. The top region, having thickness of approximately 20nm - 30

nm, is formed primarily by the particle bombardment. It is heavily oxidized and its thickness is limited by the bombardment induced sputtering. Thicker region below is relatively free of oxygen and its molecular composition is distinctly different from the original photoconductor. It is primarily formed by UV-induced cracking of the benzene rings followed by reformation of the excited radicals into new molecular species. Thickness of this region corresponds to the UV penetration depth. The possibility of preventing the formation of a parasitic surface layer will be further discussed.

10:40am **PS1-ThM9 Control of Selectivity and Profile for HfO₂ Etching in BCl₃-Containing Plasmas.** *K. Nakamura, Y. Ueda, H. Kiyokami, H. Tsuda, K. Eriguchi, K. Ono*, Kyoto University, Japan

Selective etching of high dielectric constant (high-*k*) films over the underlying Si (and/or SiO₂) is indispensable in the fabrication of high-*k* gate stacks. In practice, the selectivity is usually not so high, owing to highly volatile halogen compounds of Si, and also to strong metal-oxygen bonds of high-*k* dielectrics and less volatile metal-halogen compounds. Profile control is also indispensable during etching of high-*k*: anisotropic profiles are required for high-*k*, and also profiles of gate electrodes on high-*k* are required to remain unchanged. This paper presents the control of selectivity and profile for high-*k* HfO₂ etching under low ion-energy conditions in BCl₃-containing plasmas, with emphasis being placed on a better understanding of the etching mechanisms concerned. Experiments were performed in both electron cyclotron resonance (ECR) and inductively coupled (ICP) plasmas, by varying pressure, additive concentration of O₂, Cl₂, and Ar, rf bias power, and also substrate temperature. Samples for etching were blanket HfO₂ and TaN films, and separate Si and SiO₂ substrates were also employed for reference. Samples of TaN/HfO₂ stack as well as separate HfO₂ and TaN masked with line-and-space patterns were also employed to examine the etched profile. We examined substrate surfaces by x-ray photoelectron spectroscopy, and investigated reactant and product species in the plasma during etching by optical emission spectroscopy and quadrupole mass spectrometry. A transition from deposition to etching regimes was found to be caused on all substrate surfaces, by varying pressure, by using additives such as O₂ and Cl₂, and by increasing rf bias power. In practice, surface inhibitor deposition was less significant for HfO₂ than for Si, SiO₂, and TaN; and the threshold bias power or ion energy for HfO₂ etching was in the range 10-20 eV, while the threshold was more than 20 eV for the other. A difference in pressure, additive concentration, and bias power for the transition between HfO₂ and Si (and/or SiO₂) gave rise to high or infinite selectivity of high-*k* over Si (and/or SiO₂), together with vertical high-*k* profiles. The difference for the transition between HfO₂ and TaN also gave no significant distortion of TaN profiles during HfO₂ etching, owing to passivation layers deposited on TaN sidewalls. Plasma and surface diagnostics indicated that inhibitor species for deposition are primarily boron-chloride polymers produced in the plasma, whose concentration largely depends on pressure, additive concentration, and plasma reactor (ECR and ICP), which in turn leads to a marked difference in etching characteristics.

11:00am **PS1-ThM10 Etching Mechanisms of FeCo Magnetic Films by Chemically Reactive Energetic Ion Injections.** *K. Karahashi, T. Ito, Y. Matsumoto, S. Hamaguchi*, Osaka University, Japan

Reactive ion etching (RIE) has been widely used for semiconductor micro fabrication processes. Recently magnetic thin films have also become materials of choice for some specific microelectronics applications such as magnetic random access memory (MRAM) and read/write heads for magnetic data storage. For micro fabrication processes of magnetic films, Ar ion milling seems to be almost the only etching technique in the current manufacturing processes. However, capabilities of Ar ion milling for anisotropic and selective etching of magnetic films are severely limited and therefore new technologies of reactive ion etching for magnetic films are now seriously sought. In this study, we have focused on etching processes of FeCo alloy thin films and examined their surface reactions caused by energetic Cl⁺ ion beam injections. More specifically we have measured desorbed products and etching yields (i.e., sputtering yields) of the sample, using a mass-selected ion beam system. The ion beam system can inject mono-energetic single-species ions (i.e., Cl⁺ or Ar ions in this study) to the sample (i.e., FeCo, Fe, or Co thin film) surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with a quadrupole mass spectrometer (QMS), a temperature programmed desorption (TPD) system, and an X-ray photoelectron spectroscopy (XPS). The QMS is used for the detection of desorbed products during the ion beam injections and XPS is used for in-situ chemical analyses of irradiated surfaces. The Cl⁺ ion beams used in this study are in the range of 250-1000eV. The etching yields are determined from measured depth profiles of irradiated surfaces and ion fluxes. It has been found that the etching yields of FeCo and Fe films by Cl⁺ ion injections below 300 eV are smaller than those of Co films under the same conditions. It has been also found that iron chlorides (FeCl_x) are formed on Fe surfaces under Cl⁺ ion injections and

their amounts increase with the increasing Cl⁺ ion dose. These results indicate that the reduction of etching rate of FeCo below 500eV is caused by the formation of FeCl_x on the surface. TPD of volatile materials from Cl⁺ injected Fe surfaces has shown that FeCl_x desorbs when the surface temperature is above 600K. This suggests that the control of substrate temperature is crucial for Cl-based reactive ion etching of FeCo. We have also compared these results with physical sputtering characteristics of FeCo films by energetic Ar injections.

11:20am **PS1-ThM11 Characterizing the Effects of Etch-Induced Material Modification on the Crystallization Properties of Nitrogen Doped Ge₂Sb₂Te₅.** *E.A. Joseph, S. Raoux, J.L. Jordan-Sweet, IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, D. Miller, H.-Y. Cheng, IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr, A. Schrott, C.-F. Chen, R.K. Dasaka, IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, R.M. Shelby, IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr, Y. Zhang, IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, J.S. Washington, M.A. Paesler, G. Lucovsky*, North Carolina State Univ.

Chalcogenide-based phase change memory devices have recently garnered significant interest due to their potential scalability beyond that of conventional DRAM and Flash memory technologies.[1] Due to the stringent demands imposed by the scaling roadmap, it is becoming increasingly important to understand the effects of processing on the crystallization properties of the material since it is known that there is an etch-induced material modification layer resulting from patterning.[2] In this work, we examine chemical and structural effects of processing on the crystallization properties of nitrogen doped Ge₂Sb₂Te₅ using X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), time resolved laser reflectivity and time resolved X-ray diffraction (XRD). The laser reflectivity results indicate that upon exposure to various etch and ash chemistries the (re)crystallization speed is significantly reduced. Time resolved XRD data further show that the transition temperature from the rocksalt to the hexagonal phase is increased from 400 °C to ~ 500 °C. From depth profiled XPS and XAS measurements, we attribute this increase in crystallization time (and increase in transition temperature) to the selective removal and/or oxidation of numerous elemental species (N, Ge, Sb, Te) which alters the local bonding environment and which may result in the formation of additional phases. The relevance of these effects and their ability to potentially alter device performance will also be discussed.

[1] Y.C. Chen, C.T. Rettner, S. Raoux *et al.*, IEDM Tech. Dig., p. S30P3, 2006.

[2] E. A. Joseph, T. D. Happ, S.-H. Chen, S. Raoux, *et al.*, Symp. VLSI-Technology Systems and Applications, 2008. pg 142-143, 2008

11:40am **PS1-ThM12 Surface Properties of Plasma Treated Metal Oxides.** *K. Trevino, E.R. Fisher*, Colorado State University

Metal oxides are used for various applications including polymer adhesion, anticorrosive coatings, and catalysis. Plasma treatments have proven useful in tailoring the properties of such surfaces due to their ease of use and environmental friendliness. However, the interfacial interactions that give rise to changes in surface charge and acid/base character are poorly understood. Measurement of these properties, along with surface characterization, allows for a clearer understanding of the important chemical processes. Of particular concern is the permanency of the surface treatment, which is expected to depend on plasma type, plasma conditions, substrate, and the position of the substrate in the plasma. In this work, we have separately treated SiO_xN_y surfaces with three non-polymerizing gases (Ar, H₂O, and NH₃) and monitored surface properties as a function of plasma parameters and substrate position for a period of thirty days. Surface charge and acid/base character were measured by determination of the isoelectric point (IEP) from contact angle titration data; surface composition and morphology were also taken and analyzed by XPS and SEM. Ar-plasma treatments yielded initial IEP values of ~7, however these values are not stable over time. In contrast, IEP values for H₂O plasma treatments also increased (compared to an untreated substrate) to ~6, but stay relatively stable with age. Compositional data reveal information about the effectiveness of the treatments, and IEP data highlight the similarities and differences between the plasma systems. Results from additional metal oxides and polymer surfaces will also be presented and comparisons between systems will be made.

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