

Plasma Science and Technology

Room 302 - Session PS-FrM

Plasma Surface Interactions III

Moderator: J. Caughman, Oak Ridge National Laboratory

8:20am PS-FrM1 Flexible Organic Electronics: the Role of Plasma Deposition in Multi-Layer Permeation Barrier Technology, M. Creatore, V.I.T.A. Lohmann, M.A. Blauw, Eindhoven University of Technology, the Netherlands; **M.M. Koetse, H.F.M. Schoo,** TNO Science and Industry, the Netherlands; **M.C.M. Van De Sanden,** Eindhoven University of Technology, the Netherlands

The multi-layer system of alternated inorganic and organic layers is the state-of-the-art technology for flexible organic electronics where water vapor transmission rates down to 10^{-6} g/m²/day are demanded. Under debate is the role of the organic layer, which appears crucial in affecting the growth of the inorganic film, as well as the multi-layer mechanical performance. In this framework, plasma technology has not been yet fully explored; however, it is expected to contribute to the improvement of a multi-layer system design because of the development (and, ultimately, the control) of a polymer/ inorganic layer interphase region. In this contribution we report on the studies performed by means of in situ real time diagnostics (e.g., spectroscopic ellipsometry) during the plasma deposition of inorganic (SiO₂) moisture barrier layers on polymers (poly(ethylene, 2,6 naphthalate)), as well as during the growth of the organic (silicone-like) interlayer. The layers are deposited in an Ar-fed expanding thermal plasma, where the deposition precursors (hexamethyldisiloxane and oxygen) are injected downstream and negligible ion bombardment (< 2 eV) takes place at the substrate. In these conditions, a polymer/SiO₂ interphase region develops, attributed to a sub-surface polymer modification during the initial film growth by means of a non-depositing radical (O, OH) flux competitive with the depositing radical (Si, SiO) flux towards the substrate. The effect of ion bombardment (either delivered with an average ion energy or a narrow ion energy distribution), as provided by externally biasing the substrate, is also under investigation. Its effects on the interphase region as well as on the roughness evolution, both strictly related to the multi-stack moisture permeation and mechanical performances, will be addressed.

8:40am PS-FrM2 Effect of Chamber Wall Condition for Organic Film Etching Using N₂/H₂ Plasma, K. Oshima, T. Tatsumi, K. Nagahata, K. Shinohara, Sony Corp., Japan

We investigated the relationship between N/H plasma and the wall conditions in a dual-frequency capacitively coupled plasma system. Organic low-k film is normally etched using N-H based plasma (N₂/H₂, NH₃), which is difficult to control because the H radical density greatly depends on the chamber wall conditions. Obtaining an accurate critical dimension and suppressing damage induced by the plasma requires precise control of the low-k materials. We found that when Cu was redeposited on the chamber walls during stopper layer etching, the etch rate of the organic film was drastically decreased, presumably because the H radicals were immediately lost at the conductive surface. To clarify the reaction mechanism between H radicals and Cu, we analyzed the optical emission of H, N, and O in H₂/Ar, N₂/Ar, and O₂/Ar plasma, respectively, with varying area ratios (Ra) of Cu on the Si wafer (from 1 to 100%). The emission of H clearly decreased with increasing Ra, while the N and O radical densities did not change. We also analyzed the reaction mechanism between C-F polymer and Si. When there was C-F polymer in the chamber, both O and H radicals showed relatively low density because the polymer consumed both spontaneously. Since N radicals need ion energy to react with C-F polymer, they have less dependency on the chamber wall conditions. After the polymer was cleaned with O₂ plasma, the optical emission spectra intensity of H gradually decreased because the slight oxidation of the top electrode surface was reduced by H₂ plasma exposure, and the conductive surface started to react with the H radicals. The wall conditions thus greatly affect the H radical density. Consequently, to realize stable processes, it is important to control both the generation of H radicals due to collisions between electrons and atoms or molecules and the loss of H radicals that react with the C-F polymer or metal on the chamber wall.

9:00am PS-FrM3 Comparison of Hydrocarbon and Fluorocarbon Polyatomic Ion Beam Treatment of Polystyrene, W.-D. Hsu, I. Jang, S.B. Sinnott, University of Florida

Plasma processing is widely used to chemically modify polymer surfaces and deposit thin films. It is well-accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma. Here, the detailed chemical modifications that result from the deposition of beams of polyatomic fluorocarbon ions (C₃F₅⁺ and CF₃⁺) and hydrocarbon ions (C₃H₅⁺ and CH₃⁺) on polystyrene surfaces at experimental fluences are identified using classical molecular dynamics (MD) simulations. The simulations make use of a reactive bond-order potential for hydrocarbons that has been extended to include fluorine and an optimized MD program. Based on the predicted accumulation of ion-surface collisions and accompanying chemistry, we elucidate how the unique chemical properties of the incident ions affect surface modification. We also determine the important differences and similarities in the chemical interactions of fluorocarbon and hydrocarbon ions with the polystyrene. This work is supported by the National Science Foundation through grant number CHE-0200838.

9:20am PS-FrM4 Comparison of Surface Reactivity of CN, NH, and NH₂ Radicals during Deposition of Amorphous Carbon Nitride Films from r.f. Inductively Coupled Plasmas, D. Liu, I.T. Martin, J. Zhou, E.R. Fisher, Colorado State University

Carbon nitride films have received much attention because it has been proposed that the bulk modulus of β-C₃N₄ may be greater than that of diamond. A number of groups have subsequently attempted to deposit carbon nitride films using various plasma techniques. However, the film deposition processes and their relationships with film properties are less studied. Here, the interactions of CN, NH, and NH₂ radicals with the carbon nitride film surface during r.f. inductively coupled plasma deposition were compared using the imaging of radicals interacting surface (IRIS) technique. Surface scattering coefficients, S, were obtained for various gas compositions of N₂+CH₄ and NH₃+CH₄, and r.f. powers. The S values of CN and NH radicals range from 0-0.15 and 0.8-0.9, respectively, and show very little dependence on the gas compositions and applied power. In contrast, the S values of NH₂ decrease from 0.8 ± 0.1 to 0.4 ± 0.1 when the CH₄ fraction in the plasma is increased. The essentially 100% scatter measured for NH suggests that NH is not a major deposition precursor in these plasmas. The effects of ion energies on S values were analyzed using DC bias of the substrate. The S values show an obvious dependence on the bias voltage. The r.f. inductively coupled plasmas during the film deposition have also been characterized during the film deposition by optical emission spectroscopy and mass spectrometry. Ion energy distributions were also measured using mass spectrometry. Results indicate that energetic ions are important in surface production of the species studied with IRIS. X-ray photoelectron spectroscopy analysis of deposited films showed the N content increases with increasing the N₂ or NH₃ fractions of reactive gases. The mechanisms for film deposition in these carbon nitride systems will be discussed in light of our gas-phase, surface, and gas-surface interface data.

9:40am PS-FrM5 Real-time, Nonintrusive Monitoring of Drifting Ion Energy and Flux in a High-Density, Inductively Coupled Plasma Reactor, M.A. Sobolewski, National Institute of Standards and Technology

Measurements of the radio-frequency (rf) current and voltage applied to a plasma reactor, interpreted by plasma sheath models, provide an ability to monitor the total ion flux and ion energy distribution at surfaces inside the reactor. Such measurements are useful for monitoring drift in manufacturing or laboratory reactors when direct measurements of ion flux or energy are impossible or impractical. In this study rf measurements were used to monitor drift in Ar and Ar/CF₄ discharges in an inductively coupled, high-density plasma reactor. One source of drift in such reactors is the deposition of a conductive surface layer on the dielectric window of the inductive source. As this layer grows, a greater fraction of the source power excites currents in the layer, rather than in the plasma, resulting in less efficient operation and a reduction in plasma density and ion flux. These changes in turn affect the coupling of rf bias power into the discharge, producing changes in delivered rf bias power or voltage, sheath voltages, and ion energy distributions. Using rf measurements, the resulting changes in ion flux and energy were monitored in real time, as a surface layer was deposited. Changes in ion

Friday Morning, November 4, 2005

energies as large as 100 eV were observed. Increases as well as decreases in ion energies were observed, depending on rf bias conditions. Three different mechanisms that explain the changes in ion energies were identified. The application of the technique to monitoring process drift or irreproducibility caused by factors other than deposition on the dielectric window will also be discussed.

10:00am **PS-FrM6 Saturation of Etching Rate in Downstream Plasma Chamber Cleaning**, J.J. An, B. Bai, H.H. Sawin, MIT

NF₃ and fluorocarbon downstream plasmas were investigated to study downstream chamber cleaning system. As the flow rate of NF₃ increases, the etching rate of TEOS increases; however, the etching rate saturated at a given sample temperature. Flamm (1979) showed the etch rate of fluorine is a linear function of the density of F atoms, but did not observe the saturation regime. Under chamber cleaning conditions, the etching rate can be saturated, particularly on the walls where the temperature is lower than in the electrode region. Therefore an understanding of this phenomenon is critical to understanding the rate limiting processes for chamber cleaning. The etching rate was modeled using a physisorbed precursor state in which atomic F is weakly bound to the surface. The physisorbed F reacted with the fluorinated surface in a sequential reaction with a particular reaction step being rate limiting. The reaction model gives the expected first order response with atomic F concentration that was observed by Flamm at low atomic fluorine concentrations in which the etching rate is limited by the combination of adsorption equilibrium and reaction rate. At sufficiently atomic F concentrations, the surface becomes saturated and the etching rate is limited by the surface reaction rate alone. Using these surface kinetics, a well mixed reactor model was used to compute the cleaning of chambers in which surface areas of differing temperatures are exposed to the same atomic F concentration. The results for this model will be discussed for both NF₃ and fluorocarbon cleaning of PECVD reactors.

10:20am **PS-FrM7 Depletion of Plasma-Induced Charge on Semiconductor Dielectrics using Ultraviolet and Vacuum Ultraviolet Radiation**, G.S. Upadhyaya, J.L. Shohet, J.L. Lauer, R.W.C. Hansen, University of Wisconsin-Madison

Radiation-induced charging during the processing of semiconductor materials can adversely affect device reliability. We have reported previously that vacuum ultraviolet (VUV) radiation with energies between 7-30eV can cause ionizing collisions in the dielectric creating charge carriers, thereby increasing the dielectric conductivity. However, the most dominant form of plasma-induced damage on a semiconductor dielectric is from electron and ion bombardment. As technology progresses, is more problematic because of increasing feature aspect ratios, ions tend to collect at the bottom of high-aspect-ratio trenches while the lighter electrons crowd the trench walls, thus "shading" the ions. This electron-shading effect is not well documented due to the lack of a reliable diagnostic. In-situ techniques for depleting plasma-deposited charge will be an invaluable tool for manufacturing high quality devices. To this end, a technique for depleting plasma-induced charge by exposing plasma-charged wafers to either ultraviolet (UV) or VUV has been developed. Photons with energies ranging from 5-12eV possess sufficiently large penetration depths so as to photo-inject carriers from the substrate and thus deplete the previously deposited charge by conductive effects. Silicon wafers with silicon oxide or silicon nitride of thicknesses between 200 and 3000 Å grown on silicon were precharged to range of surface potentials of the order 4-10 volts by exposure to a 13.56 MHz RF plasma. The wafers were then exposed to synchrotron radiation with photon energies between 5-12 eV. From the comparison of the surface potential distributions before and after UV/VUV exposure, it is possible to determine the penetration depth of the VUV, the conditions for photoemission and photoconductivity, as well as the effectiveness of charge depletion as a function of photon energy and dielectric thickness. @FootnoteText@ Work supported by NSF under grants DMR-0306582. and DMR-0084402.

10:40am **PS-FrM8 Investigating the Interaction of High-Pressure, High Temperature Plasmas with Propellant Surfaces through Experimental Modeling**, R. Valliere, A. Dyachenko, R. Blumenthal, Auburn University

The electrothermal chemical (ETC) ignition of propellants has many advantages over conventional ignition, the most remarkable is a short, highly-reproducible ignition delay. ETC ignition results from the impingement of a multi-millisecond long pulse of high-pressure, high-density atomic plasma on the surface of the propellant. The plasma is generated by the nearly complete ablation of a polymer tube as a large capacitor is discharged through it. Direct determination of the chemical

and physical processes responsible for the beneficial properties of ETC ignition would require surface sensitive probes capable of penetrating a plasma pulse that has pressures up to 33 MPa and temperatures as high as 30,000 K.@footnote 1@ In the absence of suitable probes, one must find an alternative approach. An often overlooked alternative to direct measurement is experimental modeling, pioneered by Winters and Coburn.@footnote 2@ Experimental modeling consists of replacing a complex and/or impenetrable environment with one or more of its individual components, generated in a way that is compatible with traditional surface probes. In the study of plasma ignition, the challenge is to find a vacuum compatible replacement for the ETC source output. In this work, atomic plasmas with composition and pressures close to those of the plasma pulse are created by laser ablation of thin polymer films deposited directly on the surface of the propellant. The chemical products of the nanosecond-long plasma with the propellant surface are monitored by mass spectrometry and the resulting surface is examined by XPS and Auger with the results compared to those found after truncated ETC ignition. @FootnoteText@ @footnote 1@ M. Nusca, M.J. McQuaid and W.R. Anderson, J. Thermophys. Heat Trans. @bold 16(1)@,157 (2002).@footnote 2@ H.F. Winters, and J.W. Coburn, JVSTB @bold 3(5)@, 1376 (1985).

Author Index

Bold page numbers indicate presenter

— A —

An, J.J.: PS-FrM6, **2**

— B —

Bai, B.: PS-FrM6, **2**

Blauw, M.A.: PS-FrM1, **1**

Blumenthal, R.: PS-FrM8, **2**

— C —

Creator, M.: PS-FrM1, **1**

— D —

Dyachenko, A.: PS-FrM8, **2**

— F —

Fisher, E.R.: PS-FrM4, **1**

— H —

Hansen, R.W.C.: PS-FrM7, **2**

Hsu, W.-D.: PS-FrM3, **1**

— J —

Jang, I.: PS-FrM3, **1**

— K —

Koetse, M.M.: PS-FrM1, **1**

— L —

Lauer, J.L.: PS-FrM7, **2**

Liu, D.: PS-FrM4, **1**

Lohmann, V.I.T.A.: PS-FrM1, **1**

— M —

Martin, I.T.: PS-FrM4, **1**

— N —

Nagahata, K.: PS-FrM2, **1**

— O —

Oshima, K.: PS-FrM2, **1**

— S —

Sawin, H.H.: PS-FrM6, **2**

Schoo, H.F.M.: PS-FrM1, **1**

Shinohara, K.: PS-FrM2, **1**

Shohet, J.L.: PS-FrM7, **2**

Sinnott, S.B.: PS-FrM3, **1**

Sobolewski, M.A.: PS-FrM5, **1**

— T —

Tatsumi, T.: PS-FrM2, **1**

— U —

Upadhyaya, G.S.: PS-FrM7, **2**

— V —

Valliere, R.: PS-FrM8, **2**

Van De Sanden, M.C.M.: PS-FrM1, **1**

— Z —

Zhou, J.: PS-FrM4, **1**