Monday Afternoon, October 29, 2001

Plasma Science Room 103 - Session PS1-MoA

Plasma-Surface Interactions I

Moderator: S. Han, University of New Mexico

2:20pm PS1-MoA2 In-vacuo Electron-Spin-Resonce Study on Fluorocarbon Films for SiO@sub 2@ Plasma Etching, K. Ishikawa, S. Hayashi, M. Okigawa, S. Kobayashi, M. Sekine, M. Nakamura, Association of Super-Advanced Electronics Technologies (ASET), Japan; S. Yamasaki, T. Yasuda, J. Isoya, Joint Research Center of Atom Technology (JRCAT), Japan

An in-vacuo electron spin resonance (ESR) setup opens the new experimental approach to the understanding the microscopic chemical reactions in etching process. Creation of dangling bonds (DB), namely, bond breaking, is indeed a key process for etching mechanism and created DB are playing an important role for surface reactions. The in-vacuo $\ensuremath{\mathsf{ESR}}$ technique is applied to the studies of surface, on which fluorinated carbon (a-C:F) film exists, during fluorocarbon gas etching processes of an amorphous SiO@sub 2@ film. In this work, we prepared a capacitivelydriven reactor which is connected with an ESR system through a wafer transfer system. An a-C:F film was deposited on a crystalline Si substrate with 20 nm thickness which is estimated using cross-sectional transmission electron microscopy. The carbon DB signal in a-C:F film was observed after transferring to the ESR cavity under vacuum ambient. This signal are stable as long as the sample is kept in vacuum, however, once the sample was exposed to air, the signal intensity drastically decreased. The decrease of ESR intensity by air exposure points out that the oxygen molecules penetrate deeply into the a-C:F film, and terminate spin centers in the film. This technique can be applied to the reaction of a-C:F films with oxygen atoms with a bottom layer of SiO@sub 2@ films for the case of SiO@sub 2@ etching processes, the selectice etching mechanisms. @FootnoteText@ This work was supported by NEDO.

2:40pm PS1-MoA3 The Deposition on and Etching of Si(100) by Large, Hyperthermal Fluorocarbon lons, L. Hanley, E.R. Fuoco, M.B.J. Wijesundara, University of Illinois at Chicago

Fluorocarbon plasmas are commonly used to etch features into Si wafers for the production of microelectronic circuits. It has been postulated that large fluorocarbon ions participate in both etching the Si and deposition of a fluorocarbon thin film on Si that hinders etching.@footnote 1@ We study the ability of mass-selected beams of large, hyperthermal fluorocarbon ions to deposit films on and etch Si(100). 25 to 200 eV C@sub2@F@sub4@@super+@ and C@sub3@F@sub5@@super+@ ions are deposited H-Si(100) and x-ray photoelectron spectroscopy is used to analyze the resultant fluorocarbon films. The disappearance of the Si(2p) peak in the survey spectra indicates that lower energy C@sub3@F@sub5@@super+@ ions create a continuous, relatively thick film as ion fluence is increased. On the contrary, higher energy C@sub3@F@sub5@@super+@ ions create a film that is self-limiting. As the ion fluence is increased, the film thickness stays constant. The C(1s) core level spectra contain the same fluorinated carbon components at all energies. comparison of two different ions, А C@sub2@F@sub4@@super+@ versus C@sub3@F@sub5@@super+@, show close similarities in the C(1s) core level spectra leading to the conclusion that the identity of the ion does not significantly change the chemical composition of the deposition. Atomic force microscopy is also employed to view the morphology change of the different energy deposits. These results are discussed in terms of the role of large fluorocarbon ions in the plasma etching of Si(100). @footnote 1@M.B.J. Wijesundara, Y. Ji, B. Ni, S.B. Sinnott, L. Hanley, J. Appl. Phys. 88 (2000) 5004 and references therein

3:00pm **PS1-MoA4 Gas-Phase Chemistry of SiN PECVD Process at Ambient Pressure**, **G.R. Nowling**, S.E. Babayan, X. Yang, M. Moravej, R.F. Hicks, University of California, Los Angeles

The plasma-enhanced chemical vapor deposition (PECVD) of silicon nitride films has been examined in an atmospheric-pressure, helium-nitrogen discharge. The concentrations of the active nitrogen species in the afterglow have been determined by optical emission and absorption spectroscopy. For operation with 752 Torr N2 and 8 Torr He, at 32.9 (W/cm^3) RF power, and a 40.4 L/min flow rate, the plasma produced 4.8x10^15 cm^-3 of N, 2.1x10^13 cm^-3 of N2(A), 1.2x10^12 cm^-3 of N2(B), and 3.2x10^9 cm^-3 of N2(C). As the gas enters the afterglow, the concentrations of the active molecular nitrogen species drop by at least

two orders of magnitude. However, the ground-state atomic nitrogen atoms remain at a high concentration due to their slow rate of recombination by three-body collision. Spectroscopic measurements made of the gas and surface during PECVD indicate that the dominant reaction pathway is heterogeneous, i.e., occurs on the surface of the silicon nitride film. A numerical simulation has been developed which models the coupled fluid dynamics, gas-phase kinetics and surface reaction kinetics. These results together with the experimental measurements will be presented at the meeting.

3:20pm **PS1-MoA5 Study of Surface Reaction of SiO@sub 2@ Etching by Plasma Beam Irradiation**, *K. Kurihara*, *Y. Yamaoka*, *M. Sekine*, *M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for Si/SiO@sub 2@/SiN etching to achieve high etching performance. The SiO@sub 2@ etching mechanism has been studied for the last three decades by using etching reactors and beam apparatuses. Multi-beam (ions and/or radicals) experiments are useful for understanding the surface reaction by simplifying beam-surface interaction. However, the plasma surface reaction in the etching reactor is very complicated because of many kinds of ions and radicals especially for fluorocarbon gas case. We have constructed a plasma-beam irradiation apparatus to examine the plasma-surface reactions under a real etching environment. Our plasma source can control plasma parameters, such as ion energy, residence time of introduced gases, radical/ion composition, and the ratio of a neutral flux to an ion flux. Desorbed products from the SiO@sub 2@ substrate were measured by a quadrupole mass spectrometer (QMS) during CF@sub 4@/Ar gas mixture plasma beam irradiation. The desorbed products from SiO@sub 2@ are assumed to be SiFx, COFx, (x=1-3), CO, CO@sub 2@ etc. However, SiFx and COFx can not be detected separately by QMS because they have the same atomic mass. Therefore, CF@sub 4@ gas which consists of isotope C@super 13@ was used as an etching gas in order to discriminate between SiFx and COFx. It was found that major Si containing desorbed products were SiF@sub 2@ and SiF@sub 4@. Their composition, furthermore, did not strongly depend on the ion energy in the range from 300eV to 800eV. After the plasmabeam irradiation, the surface of the substrate was examined by an in-situ XPS analysis. The fluoro-carbon (CF) layers on the SiO@sub 2@ were very thin, about 0.1-0.2 nm. The thicknesses of CF layer and their properties (F/C ratio and binding states) were found to be not dependent on the ion energy. This work was funded by NEDO.

3:40pm **PS1-MoA6 Plasma Polymer Deposition and Permeation into Porous Substrates**, *S. Datta, J. Zhao, J. McDaniel,* Procter & Gamble; *S. Mukhopadhyay, P. Joshi,* Wright State University

Plasma polymerization for surface modification is gaining increased attention for industrial applications. Commercial efforts are focused, for example, on creating barrier coatings on food packaging and film-type substrates. However, another class of materials that can benefit from surface modification processes is porous substrates such as non-woven materials and woven fabrics. These materials are important for both consumer and industrial applications. Plasma polymerization is viewed as a surface modification process, that generally alters the top one micron layer of material, with no impact on bulk properties. However, for porous substrates such as fabrics and non-wovens, plasma polymerization of external as well as internal surfaces within the bulk material are important. To date, there have been few studies focused on the permeation of plasma polymerization through porous materials. This study was aimed at understanding the impact of various processing as well as substrate parameters on the permeation of plasma polymerization into porous materials. Cellulose-based filter paper was used to investigate the deposition profile and penetration of plasma treatment through porous materials. Several five or ten layer stacks of filter paper, each having different particle detention rating (different pore size) were used as model porous substrates. Plasma polymerized perfluoromethylcyclohexane (PFMCH) was deposited on these stacks and subsequent analysis of each layer in the stack was performed using X-ray photoelectron spectroscopy (XPS), contact angle measurements and water absorption rates. Correlation between these quantities will be discussed in light of the microstructure of these papers as seen by optical and electron microscopy. The dependence of plasma penetration depth upon (a) plasma parameters, (b) filter paper pore size and (c) duration of plasma treatment will be presented. @FootnoteText@ @Footnote *@J. Zhao - Current address : March Instruments, Concord, CA.

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4:00pm PS1-MoA7 Mechanisms for Surface Interactions of NH@sub x@ Radicals During NH@sub 3@ Plasma Processing of Metal and Polymer Substrates, C.I. Butoi, Primax, Inc.; M.L. Steen, E.R. Fisher, Colorado State University

The chemistry occurring at surfaces of substrates during plasma processing of polymers and metal surfaces is complex. For example, ammonia plasmas have been used to increase adhesion properties between metals and other materials and to create hydrophilic surfaces. We have examined interactions of NH and NH@sub 2@ radicals with different substrate materials during NH@sub 3@ plasma processing. NH@sub 2@ scatter coefficients, S, were obtained as a function of applied rf power (P) for polymer, silicon, and metal substrates. In most cases, S @>=@ 1, indicating NH@sub 2@ surface generation occurs at the plasma-substrate interface. Energy transfer between NH@sub 2@ and substrates was evaluated via translational temperatures for scattered NH@sub 2@ molecules, @THETA@@sub Tsc@. Translational temperatures for NH@sub 2@ molecules scattered from Pt, Cu, and Si substrates show little dependence on P, while NH@sub 2@ scattered from polymers have linear increases in @THETA@@sub Tsc@, changing by as much as ~120 K for P = 50-150 W. S and @THETA@@sub Tsc@ values measured using an ion-free molecular beam indicate ions increase both kinetic energy and amount of scattered NH@sub 2@. Examination of possible reaction pathways suggests that H atom abstraction by NH radicals may contribute to the observed surface generation of NH@sub 2@. Surface reactivity measurements for NH radicals on polymer surfaces show S < 1, consistent with this mechanism. The effects of P, substrate material and the presence of ions on NH surface interactions are presented, providing additional insight into the underlying mechanisms for NH@sub 3@ plasma processing of both polymer and metal surfaces. These surface interaction data will be presented along with mass spectral data and surface analysis, thereby providing a fairly comprehensive view of the ammonia plasma processing system.

4:20pm PS1-MoA8 Plasma Chemistry, Plasma-surface Interaction, and Surface Reactions during a-Si:H and a-SiN@sub x@:H Deposition, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands, Netherlands; E.R. Fisher, Colorado State University; E.S. Aydil, University of California, Santa Barbara; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands INVITED

Insight into the growth mechanism of plasma deposited materials is essential for full optimization and complete exploitation of the opportunities of plasma assisted deposition. Unraveling the growth mechanism requires investigation of the three different aspects of the deposition process: the plasma chemistry, the plasma-surface interaction, and the surface reactions converting surface species into bulk film. In this presentation, these three aspects will be considered and illustrated by studies on the radical dominated deposition process of hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-SiN@sub x@:H). From mass spectrometry and spectroscopic studies, the plasma species and their production and loss mechanism in plasmas of SiH@sub 4@ and mixtures with N@sub 2@ and NH@sub 3@ will be considered. From the density of the different species in the plasma their contribution to film growth has been determined. The surface reactivity and the reactions of the SiH@sub x@ and NH@sub x@ radicals on the surface will be treated as investigated by the laser-induced fluorescence (LIF) based "imaging of radicals interacting with surfaces" (IRIS) technique and the newly developed timeresolved cavity ring down spectroscopy (@tau@-CRDS). The nature of the surface during deposition and its connection with the surface reactions will be discussed using in situ attenuated total reflection infrared (ATR-FTIR) measurements of the chemisorbed SiH@sub x@ and NH@sub x@ surface hydrides. From the combination of results and the relations with the material properties, the kinetic growth models of the materials will be reviewed and further refined and extended.

5:00pm PS1-MoA10 Arc Generation from Sputtering Plasma-Dielectric Inclusion Interactions, C.E. Wickersham, J.E. Poole, A. Leybovich, J. Fan, L. Zhu, Tosoh SMD, Inc.

Arcing during sputtering and etching is a significant cause of particle defect generation during device fabrication. The size of the dielectric inclusion plays a major role in determining if arcing occurs and particle defects are generated. We studied the effect of inclusion size, material type and plasma conditions on the propensity for arcing during sputtering of aluminum targets. We have found that there is a critical inclusion size required for arcing to occur. The critical size for Al@sub 2@O@sub 3@ inclusions in an aluminum target under typical magnetron sputtering conditions is 440 \pm 160 $\mu m.$ Inclusions with sizes above this critical value readily induce arcing and macroparticle ejection during sputtering. Monday Afternoon, October 29, 2001

Inclusions below this critical size do not cause arcing or macroparticle ejection. High-speed videos were used to study the arc initiation and behavior. The effect of inclusion aspect ratio and inclusion material type such as SiO@sub 2@, TiO@sub 2@, Al@sub 2@O@sub 3@, CaO, Ta@sub 2@O@sub 5@, AIN and BN on the arcing behavior of aluminum targets were also studied. When the inclusion size exceeds the critical value the sheath over the inclusion is deformed by the charge accumulating on the dielectric inclusion and the plasma positive column distorts toward the target leading to a bipolar arc. Inclusions below the critical size do not distort the sheath to an extent great enough to permit bipolar arc formation. Our proposed model predicts that the critical inclusion size depends upon the sheath thickness, which ranged between 300 and 600 μm for the experimental conditions used in this study.

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