Thursday Morning, October 28, 1999

Plasma Science and Technology Division Room 609 - Session PS-ThM

Plasma-Surface Interactions II Moderator: S. Han, UC Berkeley

8:20am PS-ThM1 Theoretical Analysis of the Interactions of Chemically Reactive Clusters from Silane Plasmas with Crystalline and Amorphous Silicon Surfaces, S. Ramalingam¹, E.S. Aydil, D. Maroudas, University of California, Santa Barbara; W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

Silane containing discharges are used commonly for depositing hydrogenated amorphous silicon (a-Si:H). The structure and electronic properties of the film are determined by the identities and fluxes of the species that impinge and react on the deposition surface. In this presentation, we focus on the interactions with Si surfaces of bare and hydrogenated Si clusters, which can be present in significant concentrations in the plasma. We have conducted a systematic analysis, through classical molecular dynamics (MD) simulations, to study the interactions of Si@sub n@H@sub y@ clusters originating in a SiH@sub 4@ discharge with pristine and H-terminated crystalline Si (c-Si) surfaces and a-Si:H deposited on c-Si. The investigated parameters include the molecular orientation of the cluster, the impingement location on the surface, the kinetic energy of the impinging cluster, and the substrate temperature. The structures and energetics of the Si@sub n@H@sub y@ clusters predicted by the empirical interatomic potential are in good agreement with ab initio results available in the literature. The MD simulations show that the clusters react with unit probability on the pristine Si(001)-(2X1) surface and with nearly unit probability on the H-terminated Si(001)-(2X1) surface. The clusters distort considerably upon attachment to the surface. For example, the Si@sub 6@H@sub 13@ cluster contains a two-fold coordinated H atom, which frequently loses one of its bonds with a Si atom upon reaction with the surface. This leads to the formation of brush-like configurations on the surface of the film, which often collapse on the surface to form more compact structures. The high reactivity of these clusters with Si surfaces and their distortion upon reaction with the surface are explained by the strained nature of the bonds in the original gas-phase clusters. The Si atoms of the cluster often attach preferentially at the center of the dimer bond, and either weaken or break this bond.

8:40am PS-ThM2 Hydrogen Atom Reactions in a-SiC:H Film Growth, M.-S. Lee, S.F. Bent, Stanford University

The reactive hydrogen flux in plasma-enhanced chemical vapor deposition has an influential role on film growth both by acting as an excitation source and by altering growth pathways. In this work, the role of hydrogen and the evolution of hydride groups during growth and post-growth treatment of hydrogenated amorphous silicon carbon alloys (a-SiC:H) is investigated. Because the film properties depend on the hydrogen distribution in the films, understanding the hydrogen reaction pathways is important for developing control over the material properties. Thin a-SiC:H films were grown by several methods, including plasma-enhanced chemical vapor deposition (CVD) and hot-wire CVD. Methylsilanes were used as single source precursors in a low pressure regime between 200 and 600 K. In situ vibrational spectroscopy was used to provide a detailed identification of the hydride bonding in the film, and near-edge X-ray absorption fine structure (NEXAFS) provided supporting information on carbon and silicon bonding. Studies were made of the effect of H@sub 2@ dilution and postgrowth hydrogenation, using isotopic labelling. These experiments were complemented by temporal studies of deuterium exchange reactions, which were used to monitor and differentiate the elementary reactions between D atoms and SiH@sub x@ and CH@sub x@ groups in the material. Different kinetic rates and temperature dependences were observed for the reaction of D with silicon- vs carbon-hydride groups. For the SiH@sub x@ groups, rapid exchange was followed by a slower insertion mechanism; the less facile CH@sub x@ loss was not followed by a detectable increase in CD@sub x@, suggesting that etching or C=C formation may be more important for carbon. These reactions, and their temperature dependence, have important consequences for the final film structure and properties.

9:00am PS-ThM3 An In Situ Study of Plasma Deposition of Hydrogenated Amorphous Silicon Using Multiple Total Internal Reflection Infrared Spectroscopy, D.C. Marra, University of California, Santa Barbara; W.M.M. Kessels, Eindhoven University of Technology, The Netherlands; B.F. Hanyaloglu, E.S. Aydil, University of California, Santa Barbara

Multiple total internal reflection Fourier transform infrared spectroscopy (MTIR-FTIR) was used to study plasma enhanced chemical vapor deposition of hydrogenated amorphous silicon in situ and in real time. Several methods using MTIR infrared spectroscopy are combined to study the hydrogen bonding on a-Si:H surfaces as well as the spatial distributions of hydrides in the bulk film. A new technique for identifying surface adsorbates on plasma deposited films combines the sensitivity of in situ attenuated total reflection FTIR with Ar ion assisted desorption of surface species. The dependence of the silicon hydride coverage on the substrate temperature between 40 and 370@degree@C as a function of discharge power and pressure is investigated. As expected, fewer higher hydrides exist on the surface at elevated deposition temperatures. However, this observation is not universal and depends strongly on the discharge pressure and the power. In fact, the temperature dependence of the surface hydrides is less critical to the coverage than the ion bombardment. A careful study of the effect of Ar ion bombardment on a-Si:H surfaces and near surfaces has enabled experimental observation of isolated H at Si-Si bond center sites. Hydrogens at bond center sites appear to be created during deposition and are metastable. During the first 30 minutes after deposition, Si-H-Si bonds are broken and at least some of these H form more stable SiH, SiH@sub 2@and SiH@sub 3@ bonds either in the film and/or on the surface. Hydrogen concentration distribution and bonding as a function of depth in plasma deposited a-Si:H films were also studied using MTIR-FTIR in conjunction with in situ spectroscopic ellipsometry. Immediately below a hydrogen rich surface layer there is a few hundred Angstrom thick subsurface region that is depleted in H compared to the bulk film. Ion bombardment is shown to be responsible for this hydrogendepleted layer.

9:20am PS-ThM4 Plasma and Surface Chemistry in a Remote Silane Plasma Studied By Various Diagnostics and Related to a-Si:H Film Quality, *W.M.M. Kessels*², *M.C.M. van de Sanden, A.H.M. Smets, B.A. Korevaar, D.C. Schram,* Eindhoven University of Technology, The Netherlands

A remote silane plasma used for fast deposition of device quality a-Si:H has been studied in detail and information about the contribution of particular species to film growth has been obtained. The creation and fluxes of silane radicals have been studied by means of various diagnostics like appearance potential mass spectrometry (SiH@sub 3@, SiH@sub 2@,H), UV absorption spectroscopy (SiH@sub 3@) and optical emission spectroscopy (SiH, Si). From ion mass spectrometry, revealing hydrogen poor cationic clusters up to Si@sub 10@H@sub n@@super +@, in combination with Langmuir probe measurements, the downstream ion chemistry is studied. It is shown that the deposition is dominated by radicals, while the ions have a contribution of approximately 7% to film growth. The silane radicals created can be influenced by changing the plasma source operation. It is shown that the deposition of a-Si:H can be altered from a SiH@sub 3@ dominated growth to a situation in which reactive silane radicals contribute significantly. This is accomponied by a decrease of the compound value for the surface reaction probability, as determined by an aperture-well assembly, a decrease of the film surface roughness and an improvement of the film quality in terms of structural and opto-electronic film properties. The compound value of the surface reaction probability is 0.33±0.05 for the conditions in which device quality a-Si:H is obtained. The role of the specific species in film growth and their influence on film properties is discussed.

9:40am PS-ThM5 Competition Between Etching and Deposition in Methane/Hydrogen Plasma Interactions with the Si(100) Surface, H.L. Duan, S.F. Bent, Stanford University

The addition of hydrogen to alkane-based plasmas is important in a number of applications, including diamond synthesis and compound semiconductor etching. However, the mechanisms by which hydrogen influences the plasma system are not fully understood. In this study, optical and mass spectroscopic methods have been carried out to acquire a molecular level understanding of methane/hydrogen plasma interactions with a Si (100) surface. The plasma was formed via an electron cyclotron resonance (ECR) plasma source. Multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and real time in situ mass spectrometry were used to probe the time evolution of surface and gas

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species at the plasma surface interface. The results show that in the absence of added hydrogen, a polymer-like a-C:H film is deposited on the silicon surface with a linear growth rate. Addition of hydrogen into the plasma, depending on the methane-to-hydrogen ratio, can lead to a complete suppression of film growth; the steady-state coverage of hydrocarbon is about ten monolayers according to the FTIR results. At the same time, infrared absorption at the SiH stretching frequencies suggests a comparable coverage of silicon hydrides. These results together indicate that significant roughening of the silicon surface occurs, and suggest the possibility of etching. This conclusion is supported by preliminary mass spectrometric results indicating the presence of etch products during reaction. For the same plasma conditions, increasing the surface temperature increases the initial a-C:H film growth rate. However, even at elevated temperatures, growth can be suppressed by the addition of hydrogen. The experimental results indicate that there is a competition between etching and deposition chemistry determined by the methane-tohydrogen ratio in the plasma. Proposed mechanisms describing this competition, and the possibility of etching of silicon by methyl species, will be discussed.

10:00am PS-ThM6 A Multi-dimensional Model for an Inductively Coupled Ar/C@sub 4@F@sub 8@ Discharge, S. Rauf, P.L.G. Ventzek, V. Arunachalam, D.G. Coronell, Motorola Inc.

Plasmas based on complex fluorocarbons such as C@sub 4@F@sub 8@ are the main workhorse for SiO@sub 2@ etching in the microelectronics manufacturing industry. To understand the etching mechanism and how important process parameters (e.g. etch rate, uniformity) are related to typical actuators (e.g. gas pressure, power), we have recently developed a 2-dimensional model for an inductively coupled Ar/C@sub 4@F@sub 8@ discharge. The model is based on the Hybrid Plasma Equipment Model, a comprehensive plasma equipment simulation tool developed at the University of Illinois. For this project, the plasma is treated as a fluid and rates for various electron impact processes are computed using a homogeneous Boltzmann equation solver. The gas phase chemical mechanism includes electron impact ionization, dissociation and attachment processes for C@sub 4@F@sub 8@ and its C@sub x@F@sub y@ progeny, ion-ion and ion-molecule chemistry. A reasonably detailed description of surface processes at the SiO@sub 2@ coated wafer is also included. The plasma reactor model is coupled to an external circuit model. The model was used to simulate Ar/C@sub 4@F@sub 8@ based plasmas in the inductively coupled Gaseous Electronics Conference reference cell. C@sub 4@F@sub 8@ concentrations were between 10-50%, gas pressure was varied between 10-30 mTorr and total inductive power deposition was 300-700 W. Results show that most of the incoming C@sub 4@F@sub 8@ dissociates quite rapidly near the inlet into CF@sub x@ (x = 1,2,3) radicals. Substantial amount of C@sub 2@F@sub 4@ is also present in the discharge. The plasma is moderately electronegative with F@super -@ being the major negative ion. Implications of control parameters on the plasma characteristics and etching kinetics will be discussed.

10:20am **PS-ThM7 Inorganic Plasma Low-k Materials - Aurora 2.7 -**, *N. Matsuki*, Y. Morisada, Y. Naito, A. Matsunoshita, ASM Japan K.K., Japan

Methyl-SiO and Phenyl Methyl-SiO interlayer dielectric (ILD) films with dielectric constants in the 2.6 to 3.0 range were successfully obtained by PE-CVD method. Precursors used to deposit these low-k films were Dimethyldimethoxysilane Si (CH@sub 3@)@sub 2@(OCH@sub 3@)@sub 2@ and Phenylmethyldimethoxysilane Si (C@sub 6@H@sub 5@) (CH@sub 3@)(OCH@sub 3@)@sub 2@, respectively. Reaction gases consisting one of these precursors and some additive gas such as He or H@sub 2@ were introduced into the Eagle-10 reaction chamber with conventional parallel plate electrodes. These films were deposited in 400 @super o@C plasma process without an anneal step. Residence time of gas molecules in the reaction space was prolonged to enhance disintegration and polymerization in the gas phase. FT-IR data suggest that these plasma low-k films have stable Si-O network structure incorporating hydrocarbons (-CH3 or -C6H5), thus avoiding Si-OH formation. TDS and TGA data show these films have high thermal stability up to 500 @super o@C. The dielectric constant did not increase after a pressure cooker test at 120 @super o@C and RH 100% for an hour. The leakage current was found to be 10@super -9@ (A/cm@super 2@) at 2 MV/cm. The surface roughness was less than 5 nm (1µm film, P-V). The CMP rate was less than 5 nm/min using Cu CMP slurry at a Cu polishing speed of 300 nm/min. Thus, it appears that these stable low-k films have ideal properties for Cu damascene metallization insulation layers.

10:40am PS-ThM8 Plasma Modification of Polymeric Membranes, M.L. Steen, E.R. Fisher, N.E. Capps, E.D. Havey, Colorado State University Since most polymers have intrinsically low surface energy, poor adhesion and wettability severely limit many applications. The adhesion properties and wettability of polymers can be improved through plasma surface modification. The surface properties altered by plasma treatment include chemical composition, wettability and adhesion. These properties depend on the interaction of the plasma with the surface. Specifically, the plasma can often erode the polymer, abstracting atoms and breaking polymer chains. Reactive species in the plasma can interact at these active sites, thereby, implanting new functional groups. Alternatively, the plasma can also change the surface properties of the polymer by depositing a thin, conformal film on the surface. The primary goal of our research is to develop plasma-based treatments that render the surface of hydrophobic polymeric membranes permanently hydrophilic. A related goal is to investigate plasma treatments that produce highly hydrophobic materials. We have done an extensive parameter study of many plasma systems. For the hydrophilic treatments, we have studied OH implantation from pure H@sub 2@O plasmas and H@sub 2@O plasmas with a diluent gas, such as Ar. For the hydrophobic treatments, we have studied F atom implantation from CF@sub 4@ plasma. The membrane can also be rendered hydrophobic by depositing a fluorocarbon film from a pulsed CHF@sub 3@ plasma. We have also combined these two approaches by first depositing a hydrocarbon film from CH@sub 4@ and then fluorinating that film with a reactive gas, such as CF@sub 4@. Results from bubble point measurements, porometry, SEM, contact-angle measurements and gas permeability identify several plasma treatments that successfully impart these membranes with the desired surface properties. Specifically, Ar/H@sub 2@O, CF@sub 4@, CHF@sub 3@ and CH@sub 4@/CF@sub 4@ plasma treatments will be discussed.

11:00am **PS-ThM9 Polymer Surfaces Modified Using RF Plasma**, *D.A. Steele, R.D. Short,* University of Sheffield, UK; *D. Barton, J.W. Bradley,* UMIST, UK

The properties of a cold plasma are investigated using Langmuir probes and the resultant surface treatments of polystyrene studied using XPS. A glass walled reactor vessel, powered with a matched RF (13.56 MHz) supply via external excitation coil, is utilized to study the capacitively coupled plasma of argon gas. Plasma and self-bias potentials, densities and electron temperatures are investigated using compensated Langmuir probes over a range of input powers and gas pressures. At a 10W nominal input power and gas pressure of 10 mTorr the plasma has a density of 3 x 10@super 15@ m@super -3@ and an electron temperature of 2.5 eV, with an ion mean energy of almost 30 eV. Under such conditions we rationalize that, in the outermost 20Å of a polystyrene substrate, the energy deposited by ions (2.8 mW cm@super -2@) is an order of magnitude greater than that from the VUV photons. However assumptions of a model system, with a pure argon gas plasma and a polystyrene substrate free from UV absorbing impurities, have been made where the effects of residual air and desorption of water from the reactor walls are neglected. Further studies continue to determine the magnitude of these assumptions on polymer modification so a more accurate model of ion/photon energy deposition can be made.

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