Plasma Science and Technology
Room 213A - Session PS-ThA

Plasma-Surface Interaction

Moderator: G.F. Franz, University of Applied Sciences, Germany

2:00pm **PS-ThA1 A Comprehensive Study of Gas Phase and Plasma-Surface Interactions of Depositing Fluorocarbon Plasma Systems***, **I.T. Martin**, E.R. Fisher,* Colorado State University

A thorough investigation of the gas-phase chemistry, plasma-surface interactions, and surface properties of deposited materials has been performed for C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas. OES-actinometry, LIF and MS were used to study the plasma gas phase. OES quantifies excited state species in these systems, whereas LIF measurements provide relative densities of ground state CFx species as a function of applied rf power (P) and pressure. CF LIF excitation spectra were used to measure CF rotational temperatures (@Theta@@sub R@) as a function of P and pressure: @Theta@@sub R@(CF) in C@sub 4@F@sub 8@ plasmas is approximately constant over a range of P and pressure, whereas it increases with P in the C@sub 3@F@sub 8@ systems. MS data identify nascent ions and measure ion energy distributions. Plasma-surface interactions of CFx species were investigated using our Imaging of Radicals Interacting with Surfaces (IRIS) molecular beam apparatus. CF@sub 2@ surface production was characterized during C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasma processing of Si via a scattering coefficient, S(CF@sub 2@), the ratio of CF@sub 2@ molecules scattering from the surface relative to those in the molecular beam. S(CF@sub 2@) values>1 were measured during the deposition of amorphous fluorocarbon (FC) materials. This net surface production of CF@sub 2@ suggests that CF@sub 2@ is not a deposition precursor in these FC systems. Charged species contribute to CF@sub 2@ surface production, as demonstrated by the decrease in S(CF@sub 2@) measured under ion-limited conditions. A notable result of this work is the positive correlation between S(CF@sub 2@) and %-crosslinking measured by XPS in the deposited FC materials. Optimized FC materials were used in several applications, including the production of micropatterned surfaces used in cell growth studies, and the modification of microfluidic devices. The performance of our FC materials in these applications will be discussed.

2:20pm **PS-ThA2 Mechanisms of Etching in the Presence of Depositing Species: Molecular Dynamics Simulations of Silicon Etching in Fluorocarbon Plasmas***, **J.J. Vegh**, D. Humbird, D.B. Graves,* University of California, Berkeley

The fundamental mechanisms of plasma etching in the presence of depositing species, a very common situation in industrial practice, remains poorly understood at the atomistic level. Recent MD simulations of silicon etching in the presence of small FC ions and neutral radicals, F atoms, and Ar@super +@ have consistently failed to reproduce experimental observations of simultaneous Si etching and the presence of relatively thick FC film on the surface. Simulations of FC film formation alone, without Si etching, can easily be observed with small unsaturated FC ions at energies below about 100 eV, and thermal CF and CF@sub 2@ are observed to deposit alone or in the presence of low energy ion bombardment (@<=@50 eV). Si etching is observed in the presence of higher energy ions, especially Ar@super +@, and most readily in the presence of thermal F. However, the combination of significant Si etch, coupled with dominant FC signal in simulated surface XPS measurements, has proven elusive using only small FC species. Even at relatively high neutral to ion ratio (e.g. 90:9:1 CF/F/Ar@super +@), only a thin FC film develops during Si etch, and the XPS is dominated by the C-C/Si peak. We conclude that simultaneous FC film and Si etch requires heavier, unsaturated FC neutrals and/or ions. These large, polymeric species are created by ion impact or neutral F attack within a deposited FC film. In other words, the FC film can be etched in the form of large products that redeposit on the surface to maintain the film. We demonstrate that simultaneous FC film and Si etch requires that the FC film have minimal cross-linking and be relatively weakly bound to the surface. We highlight the role of ion impact in locally removing substantial amounts of FC film material, exposing the underlying Si to etch species.

2:40pm **PS-ThA3 Deposition and Composition of Polymer Films in Fluorocarbon Plasmas: CW and Pulsed Systems@footnote 1@***, **K. Rajaraman**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Fluorocarbon plasma etching is the primary method to obtain selectivity between dielectrics. Optimization of this etching technique becomes more critical as dielectrics thin. To first order, etch rates depend on thickness of the polymer layer, which controls the energy of ions striking the dielectric surface. However, the composition of the polymer determines the rate of deposition and sputtering of the film, as well as the rate of reaction of the polymer with the underlying dielectric. To address this compositional dependence, a surface chemistry model has been developed to resolve the polymer at a mesoscale level by treating CFx sites distinctly. In this manner, the fractional composition of the polymer film on a bond-to-bond basis can be resolved. This surface model was interfaced with a zero-dimensional plasma kinetics model (GLOBAL_KIN) and a 2-dimensional plasma equipment model (HPEM). Simulations were performed using the ICP reactor geometry and conditions from Li et al.@footnote 2@ We will discuss results for film compositions using different fluorocarbon gas chemistries (e.g., M/O@sub 2@/Ar, M = C@sub 2@F@sub 6@, CHF@sub 3@, c-C@sub 4@F@sub 8@). Due to the change in the pathways for generation of major free radicals, the fluorocarbon films formed in the chemistries investigated are qualitatively different, and to some degree reflect the fragmentation pattern of the feedstock gases. Changes in Ar concentration affect the amount of sputtering of the fluorocarbon films, and hence the film thickness. The consequences of pulsing the plasma on the fluorocarbon film structure will also be discussed. @FootnoteText@ @footnote 1@ Work supported by SRC and NSF. @footnote 2@ Li et al., J. Vac. Sci. Technol. A 20, 2052 (2002)

3:00pm **PS-ThA4 Dangling Bond Creation and Annihilation during Plasma Processes Studied by In-situ ESR Technique***, **S. Yamasaki**,* AIST, Japan*; K. Ishikawa,* Tohoku University, Japan **INVITED**

To understand the surface chemical reactions of plasma processes, various probes have been introduced for monitoring. Defect creation and annihilation during plasma processes, whether at surface or in bulk, play an essential role in determining final device performances and chemical reactions. If one can directly observe the creation and annihilation of dangling bond (db) centers and those dynamic changes of bonding configurations during plasma processes in real-time, it will give important information for improvement of plasma processes. In this talk we introduce in-situ ESR measurements [1,2], detecting surface defects during H2 and Ar plasma treatments on hydrogenated amorphous silicon (a-Si:H) and in-line ESR measurements during fluorocarbon gas etching processes of SiO2. From these experimental results we report how the plasma species affect surface defect structure and discuss the surface chemical reactions. [1] K. Ishikawa, et al., Appl. Phys. Lett. 81, 1773 (2002). [2] S. Yamasaki, et al., Appl. Phys. Lett. 70, 1137 (1997).

3:40pm **PS-ThA6 NH@sub x@ Radical Densities and Plasma Chemistry in a Remote Ar-NH@sub 3@-SiH@sub 4@ Plasma for Silicon Nitride Deposition***, **P.J. van den Oever**,* Eindhoven University of Technology, The Netherlands, Netherlands*; J.H. van Helden, R. Engeln, D.C. Schram, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Although plasma deposited amorphous silicon nitride (a-SiN@sub x@:H) has widespread applications in industry, the exact growth mechanism of these films from NH@sub 3@-SiH@sub 4@ plasmas remains unclear. For example, the role of silane radicals, ammonia radicals, and possibly aminosilane radicals in the growth process is still not resolved. To obtain insight into the role of the various radicals in the plasma we have carried out absolute density measurements of NH and NH@sub 2@ radicals in a remote Ar-NH@sub 3@ and Ar-NH@sub 3@-SiH@sub 4@ plasma. The radicals have been detected by means of the cavity ringdown spectroscopy (CRDS) technique probing NH and NH@sub 2@ electronic transitions at ~597 and ~335 nm, respectively. The absolute densities obtained range from 10@super 10@ to 10@super 12@ cm@super -3@ depending on the NH@sub 3@ flow, downstream axial position, and the presence and flow of SiH@sub 4@. The kinetic gas temperature determined from Doppler broadening of the absorption lines is ~1500 K, in agreement with previous measurements. For the Ar-NH@sub 3@ plasma an increase of the NH and NH@sub 2@ density with the NH@sub 3@ flow has been observed. Analysis of the data on the basis of the reaction rates proposed in literature, suggests a considerable regeneration of NH@sub 3@ from its dissociation products. This possibly explains the high NH@sub 3@/SiH@sub 4@ ratio that is necessary to obtain a sufficiently high N/Si ratio in films deposited from Ar-NH@sub 3@-SiH@sub 4@ plasmas. The addition of SiH@sub 4@ decreases the NH@sub 2@ density in the Ar-NH@sub 3@-SiH@sub 4@ plasma and at low NH@sub 3@ flows even no NH@sub 2@ is observed. To understand these trends, which can originate both from plasma and surface processes, the NH density is currently investigated under the same plasma conditions. From a comparison of the results with those obtained from a simple plug-down model, insight into the key reactions in the Ar-NH@sub 3@-SiH@sub 4@ plasma is obtained.

4:00pm **PS-ThA7 First-Principles Analysis of Precursor-Surface Interactions Relevant to Plasma Deposition of Silicon Thin Films***, **T. Bakos**,* University of Massachusetts, usa*; D. Maroudas,* University of Massachusetts

Plasma-enhanced chemical vapor deposition is used widely for growing hydrogenated amorphous silicon (a-Si:H) thin films for electronic, optoelectronic, and photovoltaic applications. Plasma deposited film properties, such as H content, crystallinity, and surface roughness, depend on the identities and fluxes of reactive radicals impinging on the deposition surface and on the corresponding radical-surface interaction mechanisms. In this presentation, we report results of first-principles density functional theory (DFT) calculations that elucidate the reaction pathways and energetics of key reactions with the H-terminated Si(100)-(2x1) surface of the SiH@sub 3@ radical, the dominant precursor for deposition of device-quality a-Si:H films. In particular, we have found that SiH@sub 3@ can insert into surface Si-Si dimer bonds, abstract H from surface Si atoms through an Eley-Rideal (ER) mechanism and passivate surface dangling bonds in exothermic and barrierless reactions. In all of these cases, we have determined the optimal reaction pathways and the corresponding transition states based on accurate, well-converged total-energy calculations and implementing the nudged elastic band method. The theoretically predicted energetics of radical insertion, H abstraction, and passivation reactions are consistent with the experimentally observed temperature independence of the SiH@sub 3@ surface reactivity during plasma deposition of a-Si:H films. In addition to the ER mechanism, we have identified a Langmuir-Hinshelwood mechanism of surface H abstraction with a moderate energy barrier that may be responsible for reducing the H content of films deposited at high temperatures. Reactions similar to those analyzed by DFT on the Si(100)-(2x1):H surface also are observed in molecular-dynamics simulations of a-Si:H thin film growth. Therefore, our electronic-structure analysis also can be considered as representative of surface reactions occurring on a-Si growth surfaces.

4:20pm **PS-ThA8 Uniformity Study in Large-Area Showerhead Reactors***, **R. Sobbia**, L. Sansonnens,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*; J. Bondkowski,* UNAXIS France SA, France

Large area plasma enhanced chemical vapour deposition of thin films such as silicon nitride or amorphous silicon is widely used for thin film transistor fabrication in the flat panel display industry. A numerical three dimensional model to calculate the deposition uniformity over the whole electrode surface for RF rectangular showerhead reactors powered at 13.56 MHz is presented. The simulation tool is a commercially-available finite-volume software (CFDRC ACE+) which solves the multi-species, multi-reaction chemistry in capacitively coupled plasma. In order to simplify the three dimensional geometry, the injected gas flow distribution across the showerhead is calculated separately and introduced as volumetric source terms for the gas flow and species continuity equations via a dynamic library coupled with the main Solver. The model is applied to the particular case of silicon nitride deposition and the results are compared with uniformity profiles obtained in an industrial PECVD reactor. Perturbations due to reactor edges together with non-uniform distribution of voltage, gas flow and chemical species are investigated as possible sources of the inhomogeneity of the thin-film.

4:40pm **PS-ThA9 Validity of Binary Collision Theory in Ion-Surface Interactions at 50-500 eV***, M. Gordon, **K.P. Giapis**,* California Institute of Technology

Ion-surface interactions in the 50-500 eV regime have become increasingly important in plasma processing. Profile evolution simulations rely on the binary collision approximation (BCA) to estimate the energy of scattered ions. Concerns exist in literature about the validity of the BCA theory at low impact energies because peculiarities are frequently seen in the scattered ion energy distribution. Sub-surface processes, multiple bouncing, and super-elastic phenomena have all been hypothesized. This talk will explore the usefulness of BCA theory in predicting energy transfer during ion-surface collisions in the 50-500 eV energy range. Well-defined beams of rare gas ions (Ne, Ar) were scattered off semiconductor (Si, Ge) and metal surfaces (Al, Mg, Ti, Ag, Au, Ni, Ga) to measure energy loss upon impact. The ion beams were produced from a floating ICP reactor coupled to a small accelerator beamline for transport and mass filtering. Exit energies were measured using a 90 deg electrostatic sector coupled to a quadrupole mass filter with single ion detection capability. Although the BCA presents an over-simplified picture of the collision process, our results demonstrate that it is remarkably accurate in the 50-500 eV range for a variety of projectile-target combinations. However, large deviations from BCA exist for combinations where electron promotions may occur during the hard collision. We find that to be the case for Si, Al, and Mg at energies greater than 500 eV. The promotion occurs at a target-dependent threshold energy and is surface mediated. Further, doubly-charged projectiles maybe generated during the hard collision at the same energy threshold. The implications of these findings for profile evolution during plasma etching will be discussed.

5:00pm **PS-ThA10 Molecular Dynamics Simulation for Physical Sputtering and Deposition of Pt and Au Films***, K. Ito,* Kyoto University, Japan*; H. Yamada,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; **S.H. Hamaguchi**,* Osaka University, Japan, Japan

Platinum (Pt) is often used as a material of choice for electrodes of submicron-scale capacitors in Dynamic Random Access Memory (DRAM) and other semiconductor devices. Gold (Au) is also used in various electronics applications due to its high conductivity and chemical stability. Since micron/sub-micron-scale etching of noble metals such as Pt and Au in semiconductor applications is usually done mostly by physical sputtering, a better understanding of the nature of beam surface interaction between non-reactive atoms and Pt/Au films may facilitate the development of better noble metal dry etching processes with higher controllability of micro-scale feature profiles. For this purpose, we have used molecular dynamics (MD) simulations to study Ar or Pt beam interaction with Pt substrates and also Ar or Au beam interaction with Au substrates, using classical inter-atomic potential functions based on the Embedded Atom Method (EAM). Especially of interest are estimates of sputtering yields/deposition rates of such processes as functions of beam energies and beam injection angles obtained from MD simulations. Some of the simulation results are in good agreement with known experimental results whereas others are qualitatively different from experimental observations although there have not been many beam experiments in the relatively low energy range that we are interested in. In this presentation, we shall present MD simulations data of the sputtering yields and deposition rates, compare those with known experimental data, and discuss possible sources of discrepancy between simulation and experimental data.

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