# Wednesday Afternoon, November 4, 1998

### Plasma Science and Technology Division Room 318/319/320 - Session PS-WeA

#### **Plasma-Surface Interactions I**

Moderator: V.M. Donnelly, Bell Laboratories, Lucent Technologies

#### 2:00pm PS-WeA1 Surface Reactions and Hydrogen Coverage on Plasma Deposited Hydrogenated Amorphous Silicon and Nanocrystalline Silicon Surfaces, D.C. Marra<sup>1</sup>, S. Ramalingam, E. Edelberg, D. Maroudas, E.S. Aydil, University of California, Santa Barbara

In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to study the H bonding on surfaces of amorphous hydrogenated silicon (a-Si:H) and nanocrystalline (nc-Si:H) films during plasma enhanced chemical vapor deposition (PECVD) from SiH@sub 4@/H@sub 2@/Ar containing discharges. During the deposition of a-Si:H films using SiH@sub 4@ without H@sub 2@ dilution, the surface coverage was primarily di- and trihydrides, and there were very few dangling bonds on the surface. In contrast, during the deposition of nc-Si:H using SiH@sub 4@ diluted with H@sub 2@, the amount of di- and trihydrides on the surface was drastically reduced and monohydrides dominated the surface. Furthermore, the vibrational frequencies of the monohydrides on nc-Si:H film match well with the resonant frequencies of monohydrides on Hterminated Si(111) and Si(001) surfaces. The decrease of higher hydrides upon H@sub 2@ dilution is attributed to an enhanced dissociation rate of tri- and di-hydrides on the surface through dangling bonds created by increased rate of H abstraction from the surface. The mechanism of hydrogen loss from the surface is thought to be abstraction by H and/or SiH@sub 3@ radicals. Simultaneously with the experiments, we have been using molecular dynamics (MD) simulations of radical-surface interactions occurring during PECVD of Si films. The MD simulations aim at the direct examination of chemical reactions, such as H abstraction by SiH@sub 3@ and by H as suggested by the analysis of the ATR-FTIR experiments. For example, using the MD simulations of deposition through SiH@sub 3@ impingement on the surface, we have observed that the dominant mechanism of H removal from the surface is through abstraction by SiH@sub 3@ radicals, which return subsequently to the gas phase in the form of silane. Atomistic simulation results will be presented together with experimental evidence for reactions that are thought to play key roles in plasma deposition of Si films.

#### 2:20pm PS-WeA2 Gas Phase and Surface Kinetics in Plasma Enhanced Deposition of Silicon Nitride: Effect of Gas Dilution on Electron Energy Distribution, Radical Generation, and Film Composition, *T.M. Klein, C.S. Yang, A.I. Chowdhury, G.N. Parsons,* North Carolina State University

Gas diluents, including N@sub@2, He, H@sub 2@, Ar, etc., are often used in silicon nitride plasma CVD to improve film density and electronic properties. We have formed silicon nitride films by parallel plate rf PECVD using SiH@sub 4@/NH@sub 3@ and SiH@sub 4@/N@sub 2@ source gases, and studied the effects of H@sub 2@, He, and N@sub 2@ dilution with substrate temperatures between 350 and 25°C. The plasma was characterized using optical emission and mass spectroscopy, and the thin films were characterized using infrared transmission, IV and CV measurements. We find that dilution can control the Si-H and N-H bond concentrations, and can improve the electrical performance in silicon nitride formed at very low temperature (35 at. %) at low temperature, resulting in high etch rates. Using SiH@sub 4@ and N@sub 2@ source gases, N/Si ratios > 1.3 can be achieved with hydrogen content < 20 at.%. However, optimized N/Si in the film is not obtained by simply increasing N@sub 2@ in the gas phase. At 12W and 250°C, increasing the N@sub 2@ gas fraction from 16% to 37%. leads to a decrease the N/Si in the film from 1.37 to 1.27. Using mass spectroscopy, the silane consumption fraction is greater than 90%, and significant change in silicon incorporation is not expected with N@sub 2@ dilution. We have modeled the effect of N@sub 2@ dilution on the electron energy distribution in the plasma using available software to solve the Boltzmann equation, and developed a simple gas kinetic model to estimate relative N and SiH@sub x@ radical concentrations. The model shows the high energy (>10eV) electron density decreases with N@sub 2@ dilution, consistent with the experiments. The model can predict the effects of gas residence time and He and N@sub 2@ dilution during nitride deposition from SiH@sub 4@/NH@sub 3@ mixtures. These results demonstrate a detailed understanding of gas

dilution effects in plasma deposition, and indicate that optimized material properties can be predicted from detailed gas reaction analysis.

#### 2:40pm PS-WeA3 Atomistic Simulation of Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon Films, S. Ramalingam, D. Maroudas, E.S. Aydil, University of California, Santa Barbara

Hydrogenated amorphous Si (a-Si:H) and microcrystalline Si grown by plasma deposition through SiH@sub 4@ containing discharges are widely used in solar cells and thin film transistors for flat panel displays. Developing deposition strategies for improving film quality requires a better fundamental understanding of the radical-surface interaction mechanisms. Atomic-scale computer simulations of the deposition process allow monitoring of the events that occur on the surface on a microscopic scale and help elucidate reaction mechanisms that lead to film deposition, defect formation and H incorporation. We present a systematic atomic scale analysis of the interactions of SiH@sub x@ (1@<=@x@<=@) radicals with pristine and H-terminated Si(001)-(2x1) surfaces as well as a-Si:H surfaces with varying H coverage. Hydrogen coverage of the surface is the key factor that controls both the surface reaction mechanism and the reaction probability. The radicals are most reactive when they impinge on pristine c-Si surfaces or surfaces of a-Si:H films with low H concentration, which have high density of Si dangling bonds. In contrast, they are less reactive on H-terminated c-Si and on a-Si:H films with high H coverage. Deposition of a-Si:H from SiH@sub 3@ radicals has also been simulated by repeatedly impinging SiH@sub 3@ radicals onto Si (001)-(2x1) surfaces. The key reactions that occur on the surface during the deposition can be grouped into three classes: (i) SiH@sub 3@ adsorption, (ii) H abstraction, and (iii) disilane formation. We have observed that the dominant mechanism of H removal from the surface is through abstraction by SiH@sub 3@ radicals, which return subsequently to the gas phase in the form of silane and leave behind a dangling bond. The dangling bond created upon H abstraction becomes an adsorption site for the SiH@sub 3@ radicals impinging at this location and the film grows by repeated abstraction and adsorption events which bring Si to surface and remove H.

#### 3:00pm PS-WeA4 The Ion-assisted Etching and Profile Development of Silicon in Molecular and Atomic Chlorine: Experiment, Modeling, and Simulation, J.A. Levinson, E.S.G. Shaqfeh, Stanford University; M. Balooch, A.V. Hamza, Lawrence Livermore National Laboratory

We report on an ion beam etching study designed to characterize the important kinetic and transport processes involved in the ion-assisted etching of silicon in both molecular and atomic chlorine. Monoenergetic argon ions were directed normal to a silicon wafer that was simultaneously exposed to a neutral molecular and/or atomic chlorine beam. Dissociation of the beam was induced by thermally heating the graphite tip of the effusive source via electron impact. Beam composition was characterized using a quadrupole mass spectrometer. Unpatterned polysilicon wafers were etched to determine the ion-induced etching yields as a function of ion energy, ion to neutral flux ratio, and neutral flux composition. A physically-based kinetic model was developed to represent the yield data. Feature etching experiments using patterned silicon wafers were also performed under ion-limited and neutral-limited conditions of varying neutral composition. Resulting profiles were examined for aspect-ratio dependent etching lag as caused by neutral starvation and/or atomic to molecular chlorine recombination. Computer simulations of the etching process and profile development were performed using the kinetic model and a line-of-sight re-emission model for the chlorine transport. The dependence of the yield on the ion angle of incidence was also incorporated into the simulation and was found to have a significant impact on profile evolution as a function of the ion to neutral flux ratio. Atomic to molecular chlorine recombination effects were explored as a function of the surface recombination coefficient. Predictions of the simulations were compared to experimentally-derived profiles.

#### 3:20pm PS-WeA5 The Role of Etching Products on the Chemical Composition and Thickness of the Chlorinated Surface Layer That Forms During Etching of Silicon in a Chlorine Plasma, K.H.A. Bogart, V.M. Donnelly, Bell Laboratories, Lucent Technologies

The influence of etching products on the surface layer formed during chlorine (Cl@sub 2@) plasma etching of unmasked and silicon dioxide (SiO@sub 2@) masked p-type Si (100) was investigated using vacuum-sample-transfer and angle-resolved x-ray photoelectron spectroscopy (XPS). The etch product concentration was controlled by varying the Cl@sub 2@ flow rate from 0.5 to 10.0 sccm at constant pressure. Gas phase Si, Cl, Cl@sub 2@, SiCl, SiCl@sub 2@, and SiCl@sub 3@ were

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monitored by optical emission spectroscopy (OES). The Si etching rate increased linearly with Cl@sub 2@ flow from 1917 Å/min at 0.5 sccm to 2848 Å/min at 10 sccm. From these rates, mass balance, and the Si area (4.62 cm@super 2@), the product-to-etchant ratio, defined as SiCl@sub x@(g)/(Cl(g) + Cl@sub 2@(g)) varied from 3.64 to 0.027 between 0.5 and 10.0 sccm, respectively, and was qualitatively confirmed by OES. On unmasked substrates, CI was present as SiCl@sub x@ (x = 1-3) at XPS Si2p@sub 3/2@ binding energies of 99.9, 101.0, and 102.0 eV, respectively, relative to Si at 99.1 eV. Surprisingly, the amounts of the three components and the total CI (also derived from its 2p peak) were nearly independent of the product-to-etchant flux ratio. Depth profiles were obtained from an inversion of the observed take-off angle dependencies of the XPS signals. The chlorinated layer was approximately 20 Å thick, with Cl falling off in a graded fashion. The Cl areal density was 2.5 x 10@super 15@ Cl/cm@super 2@ and the average stoichiometry was [SiCl]:[SiCl@sub 2@]:[SiCl@sub 3@] = 1.0:0.25:0.20. SiCl@sub 2@ and SiCl@sub 3@ were in the top 75% of the layer, while SiCl was throughout the layer. On SiO@sub 2@ masked samples, less SiCl@sub x@ was found on exposed Si sidewalls, as well as on trench bottoms, than on unmasked samples. SiCl@sub x@ coverage in the features was also independent of the product-to-etchant flux ratio, suggesting that redeposition of SiCl@sub x@ plays no role in etched profile evolution.

#### 3:40pm PS-WeA6 Reactive Ion Etching of Si by Cl, Cl@sub 2@, and Ar Ions: Molecular Dynamics Simulations with Comparisons to Experiment, *D.E. Hanson*, *J.D. Kress*, *A.F. Voter*, Los Alamos National Laboratory

We will present results of molecular dynamics simulations of reactive ion etching (RIE) of a reconstructed Si(100)(2x1) surface. The existing Stillinger-Weber Si/Cl interatomic potential has been modified by correcting the Si-Si bond strength for a SiClx moiety bound to a Si surface as a function of the number of Cl atoms, x. This potential has been used to study RIE of Si by Cl, Cl@sub 2@ and Ar ions to characterize the Si yield, product stoichiometry, and the stoichiometry of the chlorosilyl surface layer as a function of ion energy and species. Such results, suitably parameterized, can be used as fundamental input to device feature scale topography simulations. We have also simulated the dissociative chemisorption of Cl@sub 2@ on Si(100)(2x1) and find that it is in reasonable agreement with experiment. We will discuss an important area of disagreement between theory and experiment, the effect of neutral to ion ratio on the Si yield. Where possible, we will present comparisons of our results with experiment. @FootnoteText@ Work partially supported by Cooperative Research and Development Agreement between the US Department of Energy and the Semiconductor Research Corporation.

## 4:00pm **PS-WeA7** Investigation of Si-poly Etch Process for 0.1 μm Gate Patterning and Beyond, *L. Vallier*, France Telecom-CNET, France; *L. Desvoivres*, *M. Bonvalot*, France Telecom-CNET; *O. Joubert*, France Telecom-CNET, France; *S. Tedesco*, *B. Dal'Zotto*, CEA-LETI, France

The etching of dense and isolated 0.1µm gate structures has been studied in a high density plasma helicon source capable of processing 200 mm diameter wafers. The gate stack consists of 150 nm thick amorphous silicon film on a 2 nm thick gate oxide, covered with 50 nm thick SiO@sub 2@ patterns obtained using e-beam direct writing. HBr/O@sub 2@ gas chemistry is used for the etching; a 2 steps etching recipe using 2 RF bias regimes was developped in order to obtain anisotropic etching profiles without any etching anomalie(trenching, bowing, notching) while keeping a high selectivity on the very thin gate oxide. Real time ellipsometry was used either to measure etching rates or to monitor the arrival on the thin gate oxide. XPS analysis of the etched wafer is performed in an ultra high vacuum chamber after transfer under vacuum ; XPS data were obtained on dedicated structures with different aspect ratio allowing the gate oxide comsumption as well as sidewall passivation thickness to be precisely measured in dense areas. Attempts to measure CD variation due to the etch process and profiles anomalies related to the etching parameters will also be presented. @FootnoteText@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

#### 4:20pm **PS-WeA8 Mechansims in High Aspect Ratio Oxide Feature Etching using Inductively Coupled Fluorocarbon Plasmas**, *M. Schaepkens*, *G.S. Oehrlein*, State University of New York, Albany; *K.G. Donohoe*, Micron Technology, Inc.; *J.M. Cook*, Lam Research Corporation

Mechanisms controlling SiO@sub 2@ etching in high aspect ratio features have been studied using an inductively coupled plasma (ICP) source fed with trifluoromethane (CHF@sub 3@) gas. The behavior of the transition from fluorocarbon deposition to SiO@sub 2@ etching with increasing selfbias voltage has been determined in features with aspect ratios ranging from 0.8 to 6. Both the fluorocarbon deposition rate on the feature bottom at 0 W bias and the SiO@sub 2@ etching rate at highly negative self-bias voltages decrease with increasing aspect ratio. The SiO@sub 2@ etch rate reduction can be explained by a differential charging mechanism, for which experimental evidence is provided. Surface chemistry results obtained in microstructures are compared with unpatterned surfaces, and their significance for the etching process is discussed.

#### 4:40pm PS-WeA9 Surface Reactivity of CF and CF@sub 2@ Radicals Measured Using Laser-Induced Fluorescence and CHF@sub 3@ Plasma Molecular Beams, N.E. Capps, N.M. Mackie, E.R. Fisher, Colorado State University

Fluorocarbon discharges have been widely studied because of their ability to promote etching of a variety of substrates and to deposit a wide range of fluorinated polymeric films. CF and CF@sub 2@ radicals are important species in fluorocarbon pla smas and are postulated to contribute both to plasma polymerization and to selective etching of Si and SiO@sub 2@. The surface reactivity of CF and CF@sub 2@ radicals during the plasma processing of a variety of substrates using the Imaging of Radicals I nteracting with Surfaces (IRIS) technique is reported. IRIS combines spatially-resolved laser-induced fluorescence with molecular beam and plasma techniques. The molecular beam source is a 100% CHF@sub 3@ plasma, and we have investigated the surface rea ctivity of CF and CF@sub 2@ with silicon. silicon dioxide, silicon nitride, 304 stainless steel, and system 8 photoresist. Surface reactivity measurements were determined under a range of plasma powers, with ambient and heated surfaces, as well as under low and high ion bombardment conditions. On all surfaces we see generation of CF@sub 2@ radicals whereas CF radicals are consumed at the surface under similar plasma conditions. Mechanisms for film formation and for the surface production of CF@sub 2@ will be discussed

5:00pm **PS-WeA10 Optical Monitoring of Surface Adlayers by Laserinduced Thermal Desorption during Plasma Etching of Si and Ge**, *J.Y. Choe*, *I.P. Herman*, Columbia University; *V.M. Donnelly*, Bell Laboratories, Lucent Technologies

Laser-induced thermal desorption, with detection by laser-induced fluorescence (LD-LIF) and transient plasma-induced emission (LD-PIE), was used to analyze the surface during the chlorine plasma etching of Si and Ge in an inductively-coupled plasma (ICP) source. Quantitative information about the formation and ion-induced removal of this surface layer was obtained from the optical signals. A pulsed XeCl excimer laser (308 nm) was used to desorb the surface layer and (for LIF) to excite the desorbed species. LD-LIF was used to probe SiCl (292.4 nm) and GeCl (289.12 nm) to compare Si and Ge etching. The surface adlayer did not change with ion density for both Si and Ge, but the rate of adlayer chlorination for Ge was much faster (< 0.1 s) than that for Si (~ 5 s), as was indicated by the signal size when the laser repetition rate was varied. The chlorine content of the adlayer did not change with ion energy (16 - 116 eV) during Ge etching, as confirmed by XPS analysis; in contrast, for Si the adlayer became more chlorinated with increasing ion energy. The etch yield for ion sputtering from Ge increased from 1 to 3 atoms/ion from 16 to 116 eV ion energy. LD-PIE was also used to probe SiCl, SiCl@sub 2@, and Si atoms during Si etching. No LD-PIE signal from Cl or Cl@sub 2@ was detected, suggesting that steady-state chlorine desorption is negligible during the plasma etching of Si. LD-LIF and LD-PIE signals during Si etching by Cl@sub 2@ have been compared for various processing conditions. The work at Columbia was supported by NSF grant DMR-94-11504.

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