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

Plasma Damage

Moderator: C.T. Gabriel, VLSI Technology

8:20am **PS-MoM1 Mechanisms and Dependencies of Gate Oxide Degradation Due to Electron Shading**, *G.S. Hwang,* ***K.P. Giapis,*** California Institute of Technology

We present results form self-consistent Monte Carlo simulations of charging during etching of dense antennas in uniform high-density plasmas. The simulations include sheath dynamics, ion and electron transport in the trench spaces, feature charging, electron tunneling through thin gate oxides and surface charge dissipation. Charging maps are used to illustrate how electron shading causes differential microstructure charging and subsequently electron tunneling from the substrate. The magnitude of this current is employed as a measure of the extent of damage to the gate oxide. The calculations explain experimental trends regarding electron and ion temperatures and suggest ways to reduce the damage by manipulating plasma parameters. A surprising sub-linear relationship between damage and antenna area is explained by a decrease in the net ion current density collected by the structure due to charging potential changes.

8:40am **PS-MoM2 Calculation and Measurement of Ion and Electron Shading Parameters and Comparison with Computer Simulation**, ***S.C. Siu,*** *R. Patrick, V. Vahedi,* Lam Research Corporation

Electron shading is recognized as a major mechanism for plasma process induced damage in commercial plasma etch chambers. As the semiconductor industry moves to smaller feature sizes and thinner gate oxides, shading induced damage becomes a greater concern. The shading effect is known to be more severe with higher aspect ratio features and high density plasmas. Recently, V. Vahedi, et al, derived an analytic model@footnote 1@ capturing the main parameters involved in electron shading. Two of these parameters, the ion and electron shading coefficients k@sub i@ and k@sub e@, have not been measured to date, but are crucial to the model. This study uses patterned and unpatterned SPORT@footnote 2@ wafers to measure and derive these shading parameters. In addition, a PIC simulation was used to predict values for these shading parameters. The simulation is able to account for charged resist structures that cause electron shading. Comparisons were made between the simulation and the experimental results. @FootnoteText@ @footnote 1@V. Vahedi, et al, "Topographic Dependence of Plasma Charging Induced Device Damage." 2nd International Symposium on Plasma Process-Induced Damage, May 13-14, 1997, Monterey California. @footnote 2@S. Ma and J.P. McVittie, Proceedings of the Symposium on Process Control, Diagnostics and Modeling in Semiconductor Manufacturing I, 95-4, pg 401, (1995).

9:00am **PS-MoM3 Direct Experimental Determination and Modeling of VUV induced Dielectric Conduction during Plasma Processing**, ***M.V. Joshi,*** *J.P. McVittie, K.C. Saraswat,* Stanford University

The processing plasma provides a source of high intensity VUV (vacuum ultra-violet) light which is incident on IC dielectrics. It also sets up considerable electric fields across these dielectrics due to either non-uniformity or electron shading induced plasma charging. This is expected to cause photo-current flow in these dielectrics. These photo-currents can damage the underlying devices through a variety of mechanisms and change the charging profiles due to electron shading during plasma processing. Thus determination of the relationships between incident photon density, photon wavelength, applied electric field and photo-current density is vital not only to understanding and controlling photo-current damage to devices during plasma processing but also to accurately model electron shading damage mechanisms. In this work we study the photo-currents that flow through the bulk of the dielectrics as opposed to those flowing on the surface. Bulk photo-conduction would explain the damage seen during dielectric depostion in a plasma chamber. We use a high density plasma as the source of VUV light and a independent very low density plasma separate by a thin filter/window to provide the electric fields and also to act as the current source for the VUV induced photo-currents. This allows independent variation of UV intensity and plasma charging electric fields. The probe consists of a bare polysilicon pad and a nearby similar pad covered with the dielectric. These pads are biased using a voltage source and current drawn through them is measured allowing the determination of the current density - electric field characteristic for the given dielectric independent of the biasing plasma. We measured photo-current density versus applied electric field, dielectric thicknesses, dielectric types, incident photon density, incident photon wavelength, transient effects and in dual dielectrics. We propose a model to explain these effects based on hole trapping and electric field dependent hole-electron recombination cross-section in the dielectric. This model allows prediction of VUV photo-conduction damage in realistic semiconductor processing structures.

9:20am **PS-MoM4 Investigating Ion Density and Electron Temperature Effects on Plasma Damage during Pulsed and Continuous Wave Metal Etching**, ***K.H.A. Bogart,*** Lucent Technologies*; J.I. Colonell,* Praelux*; M.V. Malyshev, V.M. Donnelly, J.T.C. Lee,* Lucent Technologies

Plasma induced damage across gate oxides has been shown to decrease with the use of pulsed rf source power, although the basis for the reduction in damage is not yet well understood. During the pulsed plasma off time, positive ion density (n@sub i@@super +@), electron temperature (T@sub e@), and electron density generally decrease, reducing the current flux to the wafer and the potential difference across the substrate sheath. Near the end of the off time, negative ions are thought to cross the diminished sheath and neutralize charge on the wafer surface, and also to be the predominant negative charge carrier in the plasma. Langmuir probe measurements of n@sub i@@super +@ and T@sub e@ were made on a LAM 9600-PTX commercial metal etcher using blanket SiO@sub 2@, Al, and TiN films as well as during etching SiO@sub 2@-masked TiN/Al/Ti/TiN while reactor pressure (5-30 mTorr), rf source power (0-400 W), rf substrate bias power (0-200 W), pulse duty cycle (0.5 - 1), and pulse period (0.100 - 1000 ms) were varied. Plasma induced damage was quantified on wafers with 0.25 µm linewidth technology NMOS and PMOS damage testers etched under the conditions listed above. For a 50% duty cycle, 100 µs pulse period, typical I-V curves (asymmetric about zero current) were collected with substrate bias applied. Without substrate bias, I-V curves characteristic of an ion-ion plasma (symmetric about zero current) were observed from 0-15 µs and from 80-100 µs. I-V curves acquired with only substrate bias power (continuous RIE mode) were similar in shape to I-V curves taken at the end of the pulse off time with bias applied. T@sub e@'s decrease and then increase near the end of the off time, indicating that the substrate rf bias power is sufficient to sustain a plasma during the off time, and that negative ions are not able to cross the sheath. Implications for plasma damage mechanisms will also be discussed.

9:40am **PS-MoM5 Sources of Plasma Induced Damage in Back-End VLSI Processing**, ***S.W. Downey,*** *D.W. Hwang, N. Layadi, P.W. Mason, A. Yen, V.M. Donnelly, M.V. Malyshev,* Lucent Technologies, Bell Laboratories*; J.I. Colonell,* Praelux, Inc. **INVITED**

The possibility of plasma induced damage of devices during wafer processing exists in both etch and deposition steps using gaseous discharges. A variety of mechanisms exist for deleterious current flow through a thin (25 @Ao@) transistor gate oxide. Plasma induced damage, as measured by gate leakage currents or shifts in threshold voltages, are given for several etch and deposition processes. Device damage during metal etch is shown to be related to aspect ratio and measured electron temperature. Evidence of current or voltage-limited conditions can be extracted by modeling. Cleaning and photoresist stripping plasmas can also cause damage if not properly designed or operated. Charging of photoresist while stripping is shown to be avoidable. Damage from plasma based metal deposition tools and via etchers is also problematic and difficult to decouple. Data will show that damage is sensitive to both hardware and process parameters, but improved hardware can yield a larger damage free process window.

10:20am **PS-MoM7 Charge Density Measurements in a Metal Etch Strip/Passivation Chamber**, ***R.L. Jarecki,*** *M.G. Blain,* Sandia National Laboratories*; J.S. Papanu,* Applied Materials, Inc.

Manufacturers have increasingly incorporated chambers capable of resist stripping as well as in situ passivation of etch residues on their metal etch tool platforms to mitigate corrosion resulting from exposure to atmospheric moisture. Such chambers typically feature a downstream microwave collisional plasma source with a pressure in the 0.5 to 10 Torr range using multiple-step chemistries based mainly on O@sub 2@ (for fast resist strip) and H@sub 2@O (for passivation by chlorine scavenging). Although "downstream" plasma strip processes are usually presumed to be almost charge-free due to the rapid decay of plasma density away from the source, it may be advantageous in practice to allow some level of charge to survive in order to increase the flux of etchant species to the wafer, and hence throughput. This study reports the direct measurement of ion

current densities observed via Langmuir probe in a commercial in situ strip and passivation chamber, for various gas feeds and hardware configurations, to help assess the level of charging damage to actual devices. Wafer level ion current densities below 2x10@super -8@ A/cm@super 2@ for typical strip processes and 8x10@super -10@ A/cm@super 2@ for passivation processes were observed with a standard gas distribution baffle configuration, while modified baffle configurations resulted in somewhat higher ion currents. Increases in power or total flow rate tended to increase current density. Correlation of probe measurements to surface photovoltage and antenna structure data will also be discussed@footnote 1@. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

10:40am **PS-MoM8 Evaluation of Tests to Examine Charging Damage in Ion Implantation and Plasma Processes**, ***M.J. Goeckner,*** Varian Semiconductor Equipment Associates*; J. Erhardt,* AMD Inc.*; S.B. Felch,* Varian Semiconductor Equipment Associates*; K. Ahmed,* AMD Inc.

Charging damage is a critical issue in both plasma processing and ion implantation systems. Charging damage is typically studied with one of several distinct types of test structures. One of the more common is an "antenna" MOS capacitor test structure. After the device is subjected to the charging environment, plasma or implantation, the gate dielectric is then analyzed for damage. For this paper, we will examine three analysis techniques on various dielectrics. These analysis techniques are: measurement of temporal change in induced voltage at a low current density (dV/dt); measurement of induced leakage current at a low voltage (~2 V); and measurement of induced voltage at a high, stressing, current density (~1 A/cm@super 2@). Damage to the dielectric will be induced with a controlled damage current, of known length and strength. Dielectrics will range from 100 Å oxide to sub-40 Å nitrided oxides. The purpose of this work is to determine the most appropriate technique for characterizing plasma charging dielectric degradation in the ultra-thin dielectric regime, as well as to gain a baseline understanding of the damage under controlled conditions. It is envisioned that the results of this study can be used as a gauge for future experiments, as well as to provide an estimate of the damage currents in actual ion implantation and plasma processing environments.

11:00am **PS-MoM9 Study of Synchrotron Radiation-Induced Surface-Conductivity of SiO@sub 2@ for Plasma Charging Applications**, ***C. Cismaru,*** *J.L. Shohet,* University of Wisconsin, Madison*; J.P. McVittie,* Stanford University

During plasma processing, charging of dielectrics plays the leading role within the damage mechanisms. The charging potentials are determined by specific plasma and processed device parameters. Dielectric conductivity induced by vacuum ultraviolet (VUV) irradiation is one mechanism to affect dielectric charging not very well understood. In this work we investigate electrical surface conductivity in SiO@sub 2@ exposed to monochromatic synchrotron radiation for plasma charging applications. Special test structures were exposed to controlled fluxes of monochromatic synchrotron radiation in the range of 500 Å to 3000 Å (approx. 4 eV to 25 eV), the energy band of most plasma VUV radiation, at the Synchrotron Radiation Center, University of Wisconsin-Madison. During the exposure, radiation-induced currents in SiO@sub 2@ were monitored while controlling the electric field across the sample. Results show different characteristics of the photoinduced currents depending on the intensity of the electric field, thickness of the oxide, and radiation wavelength. Implications of these results on plasma charging of dielectrics will be discussed. This work was supported in part by the National Science Foundation under Grant No. EEC 8721545 and the Semiconductor Research Corporation under Contract No. 98-1J-106. The Synchrotron Radiation Center is a national facility, funded by the National Science Foundation under Award No. DMR-9531009.

11:20am **PS-MoM10 Effect of Surface Oxide Loss on Surface Potential Measurement (SPM) Accuracy for Plasma Charging Damage Characterization**, ***S. Ma,*** *K. Nauka, R. Kavari,* Hewlett-Packard Company

It is well recognized that the surface potential measurement (SPM) technique can be used as a process diagnostic tool for evaluating plasma-induced charging damage in MOS devices. To date, it is the simplest and cheapest non-invasive method using blank oxide wafers to monitor cumulative wafer charging after plasma exposure. Despite of its convenience, SPM's results do not always correlate well with MOS device charging damage data, especially in sputter clean, metal etch and oxide etch processes. There is limited understanding currently available to explain why the weak correlation sometimes exists. This paper examines the reason why surface potential measurement (SPM) results after plasma exposure do not always correlate to the results of plasma induced charging damage measurement on devices. One very important explanation has been found to be non-uniform surface oxide loss during plasma exposure on test wafers. From biased oxygen plasma exposure experiments in a M0RI source high density plasma etcher, the SPM results lost their correlation to antenna capacitor device damage when the substrate bias was sufficient to etch the surface oxide. As the amount of surface oxide loss increases, deposited surface charge distribution correlates better to surface oxide loss than to the damaged antenna capacitor data. Longer plasma exposure time with more oxide loss also shifts the SPM results to a higher averaged value. Compared to the device damage data, the critical surface oxide loss causing misleading SPM results is estimated to be around 70Å. Therefore, this characterization method is applicable to plasma induced charging damage for limited processes that do not cause severe surface oxide loss such as resist ashing, high oxide selectivity poly etch, etc.

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

Plasma Diagnostics I

Moderator: H.H. Sawin, Massachusetts Institute of Technology

2:00pm **PS-MoA1 Diagnostics for Insight into Fluorocarbon Plasma Chemstry*, H. Sugai,*** Nagoya University, Japan **INVITED**

Understanding and controlling high-density fluorocarbon plasmas for dielectric etching has been requiring innovative tools for plasma diagnostics. First, I present a novel and simple probe called plasma absorption probe (PAP), which enables one to measure the local electron density even when the probe surface is soiled with processing plasmas.@footnote 1@ The PAP is based on the resonant absorption of surface wave excited in a "cavity" at the probe head. Second, I describe a new technique for measuring electron energy distribution function (EEDF), i.e., RF-biased optical probe (RF-BOP).@footnote 2@ These new tools reveal a clear difference between high-density ICP and surface wave plasma in their EEDFs, radical and ionic compositions. In the latter half of presentation, I focus on plasma wall interactions. Steady-state radical density profiles near the wall suggests that radical production on surfaces often exceeds the production by electron-impact dissociation of parent molecule. To give an insight into the mechanism, the time/space resolved measurement of radical density is made in a source gas puffed out repeatedly. This experiment allows us to separate the gas phase from the surface processes in time space. Another approach of ion-beam surface experiment is challenged: an ion beam of fluorocarbon species is injected to a substrate at the energies from 10 to 200 eV, and the radicals produced on the surface are detected as a function of the ion energy. For example, SiF@sub 2@, CF@sub 2@ and CF with less CF@sub 3@ are observed desorbing from silicon surface bombarded with CF@sub 3@@super +@ ion. The relevant fluorocarbon chemistry will be discussed combining the beam study with the plasma experiment. @FootnoteText@ @footnote 1@H. Kokura, K. Nakamura, I. Ghanashev and H. Sugai, to be published in Jpn. J. Appl. Phys. @footnote 2@H. Toyoda et al., Extended Abstract of Int. Conf. Reactive Plasmas / GEC (Maui, 1998) p.27.

2:40pm **PS-MoA3 Comparison of Actinometric and Diode-laser Absorption Measurements of [CF] and [CF@sub 2@] in an Inductively Coupled Plasma Reactor*, T.M. Bauer,*** *A. Inoue, P.-T. Ton-Nu, J.L. Cecchi,* University of New Mexico

CF and CF@sub 2@ radicals have been shown to be significant precursors for selective oxide etching. Consequently, diagnostics that measure concentrations of these radicals are of interest for process development, monitoring, and control. We compare two such diagnostics: actinometry and wavelength-modulated diode laser absorption spectroscopy. Actinometry is a relatively simple technique. However, it relies on excited state species measurements and may suffer from unwanted influence from other plasma parameters. The diode laser is a more complicated technique, but it provides absolute ground state concentrations. To carry out these comparisons, we have made actinometric and diode laser measurements contemporaneously on an ICP reactor over a pressure range of 10 to 30 mTorr and rf power range of 200 to 1000 W. Gas feedstocks included C@sub 2@F@sub 6@, CHF@sub 3@, and CF@sub 4@, each with 10% Ar added as an actinometer. Over these ranges, the CF concentration varied from 8x10@super 12@ to 4x10@super 13@ cm@super -3@, as determined by the diode laser. The CF@sub 2@ concentrations ranged from 5x10@super 13@ to 9x10@super 14@ cm@super -3@. Our results indicate that for CF@sub 2@ concentrations greater than 8x10@super 13@ cm@super -3@, the actinometric measurements are proportional to the absolute concentrations measured with the diode laser system, with the same constant of proportionality for all feedstocks and over the entire operating range. For CF@sub 2@ below 8x10@super 13@ cm@super -3@, we observe some deviation of the actinometric data, possibly due to interference from other features in the spectrum. For CF, we find that actinometric measurements are proportional to the absolute concentrations measured by the diode laser as a function of power, however, the constant of proportionality depends strongly on pressure and to a lesser extent on the feedstock. We believe that this reflects an underlying dependence of the CF actinometric signal on electron temperature.

3:00pm **PS-MoA4 Ion Energy Distribution Functions (IEDFs) in NF@sub3@ based Discharges with Various Diluents*, H. Hsueh,*** The Pennsylvania State University*; B.S. Felker,* Air Products and Chemicals, Inc.*; R.T. McGrath,* The Pennsylvania State University*; J.G. Langan,* Air Products and Chemicals, Inc.

NF@sub 3@ based discharges are commonly used for cleaning residual SiO@sub 2@ and Si@sub 3@N@sub 4@ films formed on the walls of PECVD chambers. In order to find a balance between fast chamber cleaning and overly aggressive cleaning chemistries, which can lead to premature hardware failure, a fundamental understanding of the physical and chemical characteristics of the discharge is required. For this reason, we have measured the relative concentration of the ionic and neutral species, ion energy distribution functions (IEDFs), and the optical emission spectra (OES) present within capacitively coupled parallel plate discharges operated with NF@sub 3@ diluted with either Ar, He, Ne, or O@sub 2@. For reactor operation at a fixed power density of 1.35 W/cm@super 2@ and various NF@sub 3@ mole fractions, we found that when Ar was used as the diluent, the principal ion present was Ar@super +@ for all pressures investigated (0.5-1.5 Torr) and the IEDFs exhibit the highest average energies for all gas mixtures studied. In contrast, for similar reactor operating conditions using helium dilution, He@super +@ concentration was relatively low, with NF@sub 2@@super +@, F@super +@, F@sub 2@@super +@, and N@sub 2@@super +@ all having larger concentrations and the IEDFs for all species have lower energy peaks. When oxygen is used as the diluent, NO@super +@ is the major dominant positive ion species. The IEDFs are also lowered when oxygen is used. A summary of how changes in pressure and gas mixture affect IEDFs for all of the diluent options mentioned above will be presented. Optical emission spectra were also recorded as a reference for all of the discharge conditions investigated.

3:20pm **PS-MoA5 Optical Emission Thermometry Applied to the Measurement of Neutral Gas Temperature within a High-density, Inductively-coupled Plasma Abatement Device*, D.B. Graves, E.J. Tonnis, M.W. Kiehlbauch,*** University of California, Berkeley

Flowing plasma reactors have proven important as downstream sources of reactive species and show promise for applications such as abatement of perfluorocompounds and other environmentally harmful effluents produced by the semiconductor industry. Recent spectroscopic measurements and simulation predictions in a inductively-coupled plasma source indicate that at high input powers, the neutral gas temperature within the plasma zone can be many times higher than ambient (> 1500 K) depending upon the plasma chemistry. High neutral-gas temperature could alter the dominant chemical mechanisms in the plasma and it is therefore important to measure and compare these results to model predictions. In this work, the neutral temperature of flowing CF@sub 4@/O@sub 2@, C@sub 2@F@sub 6@/O@sub 2@, and CF@sub 4@/H@sub 2@O plasmas was measured at varying input conditions using optical emission thermometry techniques. It was found that the rotational temperature, which was assumed to thermalize with translational temperature, is sensitive to the chemical nature of the plasma. In particular, C@sub 2@-derived (516.5 nm) emission temperatures measured within a CF@sub 4@/O@sub 2@ plasma were estimated at greater than 2000 K, which is several times higher than N@sub 2@-derived (399.8 nm) temperatures (~500 K) observed within a pure N@sub 2@ discharge over the same range of pressures and powers. In addition, the rotational temperatures were found to be relatively insensitive to the input power as long as a high-density discharge was sustained.

3:40pm **PS-MoA6 Using Optical Emission Spectroscopy (OES) to Monitor Different Parameters for a Contact Hole Etch Process between Wet Clean*, D. Knobloch,*** Infineon Technologies Dresden GmbH & Co. OHG, Germany*; F.H. Bell,* Infineon Technologies AG, Munich, Germany*; J. Zimpel, K. Voigtlaender,* Fraunhofer Institute, Germany

Oxide etch processes in IC-fabrication is gaining more and more importance, since the open area of contact hole processes still decreases and metal etch processes become partly replaced by the dual damascene technology. However, process development and stability issues in a manufacturing environment is still handled by trying to adapt a well known base line process on new applications. A typical example is the use of design of experiments in order to determine the robustness of the process window. We established a plasma monitor module for oxide etch processes to simplify process development, characterize process drifts, investigate process mix, and optimize endpoint detection. The monitor module is based on an optical multi-channel analyzer system that allows simultaneous detection of wavelength ranges between 200-950 nm. The

system can be coupled to etch tools via the host net to collect data on a run to run basis. Intelligent data analyses software, such as principa! l component analysis (PCA) and partial least square (PLS) algorithms, is implemented to extract process and equipment relevant parameters. A typical manufacturing issue is the mean time between clean (MTBC) of oxide etch equipment. In general, wet cleans are conducted in case particles or the etch rate non-uniformity exceed certain specifications. Indeed, for the etch chamber under investigation, the decrease of the oxide etch rate at the wafer edge determines the wet clean cycle. We analyzed oxide and silicon surfaces after etching as a function of rf-hours and on different spots of the sample using x-ray photoelectron spectroscopy (XPS). The results show that the etch rate non-uniformity can be correlated to the polymer composition. Moreover, the optical emission data show that analysis of suitable wavelength ranges can be used for physical interpretation of the non-uniformity phenomenon. Furthermore, the influence of process mix on the cleanliness of the etch chamber will be discussed.

4:00pm **PS-MoA7 Radical Detection using Appearance Potential Mass Spectrometry*, H. Singh**, J.W. Coburn, D.B. Graves,* University of California, Berkeley

Appearance potential mass spectrometry (APMS) has recently gained importance for quantitative measurements of reactive radical species in plasmas. We have characterized the contributions to the APMS signal from the line-of-sight "beam" component and the background component of the species in the ionizer of the mass spectrometer. The beam signal is proportional to the number density of the species in the plasma, while the background component of the signal depends on various factors like the vacuum system design and pump speeds. Single stage differential pumping of the mass spectrometer is generally inadequate as the background signal usually dominates the beam signal for both radical and stable species. This necessitates implementation of modulated beam mass spectrometry using a mechanical chopper in the beam path. With one stage of differential pumping, the uncertainty in the beam component measurements is found to be as large as ±180 %. High beam to background signal ratio (>1.0) is achieved using three stages of differential pumping, and this vastly reduces the uncertainty in the beam component measurement to less than ±10 %. Another source of error in the APMS measurements is due to the lower extraction efficiency of the hot fragment ions produced by dissociative ionization in the ionizer of the mass spectrometer. The collection efficiency of the hot fragments is found to be up to 15 times smaller than that of products of direct ionization. The use of the dissociative ionization signal under plasma-off conditions to calibrate the radical direct ionization signal thus leads to overestimation of the radical number density, and we recommend an argon reference signal to avoid the discrimination effects due to dissociative ionization. The combination of multiple stages of differential pumping, background subtraction, and use of a direct ionization reference signal allows accurate quantitative measurements of radical density at the beam sampling point using APMS.

4:20pm **PS-MoA8 C@sub 4@F@sub 8@ Dissociation Rate Control for Oxide Etch Process Plasma by Changing EEDF*, S. Noda**, T. Tatsumi, N. Ozawa, K. Adachi, M. Okigawa, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

In a dry etching process of SiO@sub 2@, optimizing the fluxes of chemical species and ion energy is essential to achieve high etch performances. The dissociation rate of reactive gas is one of the important parameters that can be used to control the density of the chemical species, i.e. radicals and ions, and their composition in the gas phase. In Ar based C@sub 4@F@sub 8@plasma in a dual frequency parallel plate reactor system,we showed that the radical density ([CFx]) and the composition ([F]/[CFx]) were well correlated with a relation "@tau@ n@sub e@ <@sigma@v>" (@tau@: gas residence time, n@sub e@: electron density, and <@sigma@v>: dissociation rate coefficient (a function of electron impact dissociation cross section and electron energy distribution function (EEDF)).@footnote 1@ The dissociation rate could be easily controlled by choosing a gas flow rate (@tau@) and a source rf power (n@sub e@) at a constant <@sigma@v> value. For further control, we need to know the effects of the <@sigma@v> which is varied by the EEDF depending on discharge conditions and types of plasma sources. We investigated if the control of dissociation rate and radical density in the gas phase would be possible by changing the EEDF. We employed a C@sub4@F@sub 8@ gas dilution with Xe gas that has a lower ionization threshold energy than Ar. The EEDF profile was determined by the relative intensity method using optical emission spectroscopy (OES).@super 2@ In the Xe based plasma, the EEDF profile was much different from that in the Ar based plasma. The density of high energy-electron (>10 eV) was about ten times lower than that of Ar based plasma at the same n@sub e@ (4 x 10@super 11@ cm@super -3@) and@tau@ (6 msec). It was also confirmed that the dissociation rate of both plasmas were followed by the relation "@tau@ n@sub e@ <@sigma@v>". We conclude that the dissociation rate of reactant gas can be controlled by EEDF and the EEDF monitor may be a preferable way to control the radical composition in CF plasmas. This work was supported by NEDO. @FootnoteText@@footnote 1@T.Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998) 2394. @footnote 2@S.Noda et al., Proc. 20th Symp. on Dry Process, Tokyo (1998) p.235

4:40pm **PS-MoA9 Plasma and Surface Diagnostics in Cl@sub 2@/O@sub 2@ Discharges in Transformer Coupled Plasma Reactors*, E. Edelberg**, Lam Research Corporation*; S. Ullal, A. Godfrey,* University of California, Santa Barbara*; V. Vahedi, J.E. Daugherty, N. Benjamin, A. Perry, D. Cooperberg, R. Gottscho,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Plasma etching with high density transformer coupled plasma (TCP) reactors has become a ubiquitous process in microelectronics because of its ability to transfer patterns from a mask onto an underlying film with precision unequaled by any of the other etching methods. TCP reactors are operated at low pressures where the mean free paths of species are comparable to reactor dimensions. Thus, the role of walls and surface reactions has increased over the role of gas phase reactions in determining the plasma properties and etching behavior. This is most apparent when a stack of thin films of different materials must be etched sequentially in the same reactor using different gases. Chemicals used for etching one material adsorb onto the walls and contaminate the plasma in the following steps and may have deleterious effects on etching of other materials in the stack. In this study, we have explored the effects of wall adsorbates on the plasma properties. The objective is to understand how chemicals adsorbed on walls during one etching step affect the plasma properties in the following steps. Silicon trench isolation using Cl@sub 2@/O@sub 2@ plasmas is taken as a model process and plasma properties and their dependence on the wall conditions were studied through multiple plasma and surface diagnostics including, downstream Fourier transform infrared spectroscopy, in situ multiple total internal reflection Fourier transform infrared spectroscopy, optical emission actinometry, and Langmuir probe.

5:00pm **PS-MoA10 Oxide Etch Studies in an Inductively Coupled GEC Reference Cell C@sub 2@F@sub 6@ Discharge using Diode Laser Spectroscopy*, W.L. Perry**, H.M. Anderson,* University of New Mexico

An inductively coupled GEC Reference Cell has been modified to allow etching of patterned oxide wafers under conditions typical of commercial high density plasma reactors. This study reports on the oxide and photoresist characteristics of the tool as a function of reactor source power, bias power, pressure and heated silicon ring temperature. Diode laser absorption spectroscopy (DLAS), optical emission spectroscopy (OES) and Langmuir probe measurements were made at the same time. These measurements are used to construct response surface models of the tool's plasma chemistry behavior versus oxide and photoresist etch rate behavior. The oxide and photoresist etch rate behavior was found to also be profoundly influenced by the temperature of the cooling wafer chuck, so this became a fifth variable in the study. In a C@sub 2@F@sub 6@ discharge, CF and CF@sub 2@ radical concentrations measured by DLAS were also found to be highly dependent on wafer chuck temperature. In a 6 mTorr C@sub 2@F@sub 6@ discharge at 350 W source power and 75 W bias power, typical CF and CF@sub 2@ concentrations were in the range of 1x10@super12@ cm@super -3@ and 3x10@super 13@ cm@super -3@ range. However, if the wafer temperature is allowed to rise toward 100 C, the CF@sub 2@ concentration increases dramatically apparently due to greater photoresist interaction with the plasma. If the wafer is properly cooled, the oxide and photoresist etch rates appear to be dominated by bias power and at low bias power, net deposition of fluorocarbon polymer prevails over net etching. However, with increased wafer temperature, both power and bias exert a strong influence on film etch rates and etching occurs at even zero applied bias power. The data is expected to provide an important database for models of oxide etching in inductively coupled plasma tools. This project was funded by SEMATECH.

Plasma Science and Technology Division
Room 4C - Session PS-MoP

Poster Session

PS-MoP1 A-Si:H Film Deposition Using Plasma CVD with Suppression of Cluster-Size Particles, ***M. Shiratani***, *S. Maeda, Y. Matsuoka, K. Tanaka, K. Koga, Y. Watanabe,* Kyushu University, Japan

In order to deposite high quality a-Si:H at a high rate using SiH@sub 4@ RF discharges, we have developed methods for suppressing cluster-size particles, which are believed to degrade film quality. We have examined effects of pulse modulation of discharges, heating of the GND electrode as well as H@sub 2@ dilution on growth of particles by using two novel in situ methods@footnote 1,2@ for determination of size and density of cluster-size particles below 10 nm in size. Even under so-called device qualtiy conditions, particles have begun to be observed around the plasma/sheath boundary near the RF electrode and mainly grow in the same region. They grow at a growth rate of 10 nm/s, much higher than a typical film deposition rate of 0.1 nm/s, and their density is above 10@super 10@ cm@super -3@. We also have studied effects of GND electrode heating on suppression of particles in modulated discharges. While the modulation without heating the GND electrode brings about suppression of particle growth, the modulation with heating the GND electrode to 200C realizes deposition without cluster-size particles during more than 1 hour even for a relatively high duty cycle of 63% (t@sub on@=5 ms). This notable suppression of particle growth with the heating can be explained by a model taking account of thermophoretic force exerted on particles. High H@sub 2@ dilution (>80%) has been revealed to be effective in suppressing growth of cluster-size particles especially around the plasma/sheath boundary near the RF electrode. Correlation between particle density and film quality will be presented. @FootnoteText@ @footnote 1@M. Shiratani and Y. Watanabe., Rev. Laser Eng., 26 (1998) 449. @footnote 2@T. Fukuzawa, et al., J. Appl. Phys., 80 (1996) 3202.

PS-MoP2 Surface Reactivities of Radicals in Fluorine Containing Plasmas, ***C.I. Butoi***, *E.R. Fisher,* Colorado State University

Fluorocarbon plasmas have a variety of applications such as generation of interlevel dielectric films and etching in the microelectronics industry, as well as generation of polymeric biocompatible materials. Understanding deposition and etching mechanisms is a difficult task given the complexity of plasma systems. Using the imaging of radicals interacting with surfaces (IRIS) technique, we are able to investigate the behavior of one plasma species at a time. Hexafluoropropylene oxide (HFPO) has shown great promise for generating high CF@sub 2@ content films, and CF@sub 2@ radicals have been postulated as the main deposition precursors. Thus, studying the reactivity of CF@sub 2@ radicals impinging on surfaces is of the utmost importance in understanding film formation mechanisms. In the IRIS experiments, CF@sub 2@ spatially resolved LIF signals are collected and analyzed using a geometrical simulation of the experiment. Fitting the experimental data to simulated fits generates scatter values, S, for CF@sub 2@ radicals. S values less than 1 indicate loss of CF@sub 2@ moieties at the substrate surface, whereas S > 1 suggests surface generation of CF@sub 2@. In CW HFPO plasmas, S values of 1 were calculated for silicon based and polymeric substrates regardless of the rf power employed. Pulsed plasmas were also used and duty cycles were varied. A decrease in the CF@sub 2@ scatter coefficients was observed for both substrates tested at all duty cycles. Also, the CF@sub 2@ S values were determined when a grounded mesh was placed in the path of the molecular beam in order to probe the possible role of ions generated in the plasma. Decreases in S were observed under these conditions. To further investigate ion effects, silicon substrates were biased at +200V, which resulted in S 0.5-0.6. Additional results for plasma etching systems will be presented.

PS-MoP3 Studies on SiF@sub x@ Radicals in Fluorosilane Plasmas Used for Silicon Etching and Deposition, ***K.L. Williams***, *C.I. Butoi, E.R. Fisher,* Colorado State University

Fluorosilane plasmas are used in the microelectronics industry for etching of Si/SiO@sub 2@ and for deposition of fluorinated silicon-based materials (a-Si:H,F). Currently, fluorinated a-Si films are used in the fabrication of solar cells, photoreceptors, and thin film transistors. In spite of such high quality film production, there is still controversy over the mechanistic aspects of etching and deposition processes. Moreover, fundamental chemical information on plasma species such as SiF@sub x@ radicals is not available. Here, the surface reactivity of SiF@sub 2@ radicals during plasma processing of a silicon substrate using the imaging of radicals interacting with surfaces (IRIS) technique is reported. The molecular beam sources are 100% SiF4, 90/10 SiF4/H2, and 50/50 SiF4/H2 plasmas. Preliminary results show scatter ratios of 2.36 ± 0.08, 2.78 ± 0.08, 2.79 ± 0.13, and 3.08 ± 3.08 ± 0.11 for 30 sccm, 80 W and 170 W, and 15 sccm, 80 W and 170 W, SiF@sub 4@ plasmas, respectively. Scatter ratios >1 indicate SiF@sub 2@ is generated at the surface. Significant decreases in SiF@sub 2@ scatter are observed for SiF@sub 2@/H@sub 2@ plasmas. With these plasmas, SiF@sub 2@ scatter ratios are 1.31 ± 0.08 (10% H@sub 2@, 80 W), 1.48 ± 0.10 (10% H@sub 2@, 170 W), and 2.44 ± 0.13 (50% H@sub 2@, 170 W). These results are correlated with data from surface characterization by Fourier transform infrared spectroscopy (FTIR) and profilometry of films deposited under various plasma parameters (applied rf power, pressure, and % H@sub 2@ addition), as well as optical emission spectra for the fluorosilane plasmas studied.

PS-MoP4 Boron Effects on SBT Etching with Ar/Cl@sub 2@/BCl@sub 3@ Plasma, ***J.W. Seo***, Chung Ang University, Korea*; W.J. Lee, B.G. Yu,* ETRI, Korea*; K.H. Kwon,* Hanseo University, Korea*; G.Y. Yeom,* Sung-Kyun-Kwan University, Korea*; C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

Among the ferroelectric thin films that have been widely investigated for FRAM(ferroelectric random access memory) applications, SrBi@sub 2@Ta@sub 2@O@sub 9@ thin film is appropriate to memory capacitor materials for its excellent fatigue endurance. However, very few studies on etch properties of SBT thin film have been reported although dry etching is an area that demands a great deal of attention in the very large scale integration of ferroelectric thin film capacitors for FRAM applications. In this study, inductively coupled plasma(ICP) etcher was used for high density plasma etching of SrBi@sub 2@Ta@sub 2@O@sub 9@/Pt/Ti/SiO@sub 2@/Si with Ar/Cl@sub 2@/BCl@sub 3@ gas chemistries. SBT thin film was prepared with sol-gel method. Etch properties, such as etch rate, selectivity and profile, were measured according to split process parameters including RF power, bias voltage, chamber pressure and gas mixing ratio. Chemical reaction and residue of etched surface was analyzed with XPS(X-ray photoelectron spectroscopy) and SIMS(Secondary ion mass spectrometry). Changes of chemical composition in the chamber was analyzed with OES(Optical emission spectroscopy). As mole fraction of BCl@sub 3@ varied, boron effects with respect to residue, selectivity and etched profile was investigated. SBT was dominantly etched by Ar bombardment. Selectivity to photoresist(PR) or SiO@sub 2@ increased as decreasing mole fraction of Ar gas. Additive BCl@sub 3@ enhanced selectivity, profile and relative etch rate. SEM(Scanning electron microscopy) was used for examination of patterned SBT thin film. Change of stoichiometry on the film surface is discussed by comparing with OES analysis.

PS-MoP5 Characterization of Inductively Coupled Discharges in C@sub 2@F@sub 6@ and CHF@sub 3@, ***G.A. Hebner***, Sandia National Laboratories

The chloro-fluorocarbon gases C@sub 2@F@sub 6@ and CHF@sub 3@ are used in a number of microelectronic plasma processing systems for both oxide etch and surface passivation. To provide data on the fundamental plasma characteristics as well as plasma species, microwave interferometry has been used to measure the line integrated electron density, photodetachment spectroscopy was used to measure the negative ion density, and laser induced fluorescence (LIF) was used to measure the spatially resolved CF density. The measurements were performed in a GEC rf reference chamber with an inductive coil plasma source and rf wafer bias. Photodetachment measurements of the negative ions as a function of wavelength are consistent with the dominant negative ion being F-. Different trends between the negative ion density and the electron density show that the negative ion precursor species density depends on power, pressure and rf wafer bias, but not on the feed gas. By pulse modulating the plasma power, negative ion - positive ion recombination rates have been determined. Spatially resolved LIF measurements show the CF density peaking in the center of the C@sub 2@F@sub 6@ discharge but a more uniform radial distribution in CHF@sub 3@. CF density scaling with power, pressure, rf bias and surface material will be shown. This work was performed at Sandia National Laboratories and supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000).

PS-MoP7 Antennas for Large-Area, Inductively-Coupled Plasmas, ***M.M. Patterson***, University of Wisconsin, Madison, US*; A.E. Wendt,* University of Wisconsin, Madison

Uniform plasma processing for large and noncircular substrates motivates the examination of design alternatives to the standard spiral antenna for inductively coupled plasmas. In addition to being unsuited for rectangular

substrates, scaling of the spiral design suffers from several complications including increased voltage requirements@footnote 1@ (and therefore increased capacitive coupling). In addition, standing wave current variations along the length of the antenna exacerbate azimuthal nonuniformities along the increased spiral length.@footnote 2@ Therefore, we explore the feasibility of low inductance, scalable alternatives to the spiral design. We have constructed several rectangular antennas, 20 cm by 30 cm, from straight conductor segments, including serpentine and ladder shaped configurations. In the ladder configuration, neighboring parallel antenna segments carry currents in the same direction, while in the serpentine configuration, neighboring segments carry currents in opposite directions. Langmuir probe measurements of the spatial profiles of plasma properties show significant differences in the magnitude and uniformity of plasma density in argon discharges produced by these antennas. We will also present results from a circular serpentine antenna. Finally, as a means of understanding the differences between the antenna configurations, we have created and will present a simple model of the interference between the electromagnetic fields of neighboring parallel antenna segments. @FootnoteText@ @footnote 1@Jaeger EF, Berry LA, et al, Physics of Plasmas 2(6), 2597 (1995). @footnote 2@Kushner MJ, et al, J. Appl. Phys. 80(3), 1337 (1996).

PS-MoP8 Optical Emission and Mass Spectroscopic Studies of Reactive Species in an ICP Based Neutral Source for Ashing Processes, ***X.M. Tang***, *D.M. Manos,* College of William and Mary

In this paper, we report measurements of particle composition and flux in downstream neutral cleaning processes in a reflection-neutral source, with a comparison to pulsed plasma processes. For Ar, O@sub 2@, and CF@sub 4@ mixtures, species in the both the plasma source and neutral process region are characterized by electrostatic probes, mass spectrometry, and optical emission; in the downstream region, calorimeter (energy) probes, and a micro-torsion (momentum) balance are used to discriminate the ion, photon, and neutral fluxes. The rf power, gas composition, reflector bias, discharge pressure have been varied in this study. The results show that in the downstream region, for Ar + O @sub 2@ plasmas, neutral O atom density and flux increase with increasing power from 100 to 500 watts, and also increase with increasing pressure. Ion species, including atomic and molecular ions, decrease in the downstream region as power and pressure increase over the same range. Both optical emission and mass spectral results show that the ratio of O/Ar increases sharply as the rf power increases above 200 watts in our source. In this source, neutral translational energy is varied by variation of the bias on the reflector plate. A concern in such a source has been that the variation of reflector bias may alter the species ratios in the source. The results of this study show that this is not the case. Using the combined diagnostic set, we have been able to differentiate the energy flux contributed by neutrals, photons, and charged particles striking the substrates. Our quantitative measurements indicate that the neutral flux is somewhat higher than predicted by our earlier simulations. This paper reports refinements to the model@footnote 1@ required to account for these new measurements. @FootnoteText@@footnote 1@ C.A. Nichols and D. M. Manos, J. Appl. Physics, vol.80 No.5 P2463.sept. 1996.

PS-MoP9 Estimation of Surface Kinetic Parameters and 2D Simulation of InP Pattern Features during CH@sub 4@-H@sub 2@ Plasma Etching, ***A. Rhallabi***, *L. Houlet, G. Turban,* University of Nantes, France

Dry etching pattern-transfer of III-V materials from resist mask is an essential process stage in the fabrication of optical devices because anisotropy and reproducibility are more ensured than that in wet etching as feature dimensions decrease. In this study, 2D model of InP etched surface profile under CH@sub 4@-H@sub 2@ plasma is developed. In order to move the InP etched surface, an improved string algorithm is applied. The surface is approximated by a series of nodes joined by straight line segments which define the surface elements or string. During the displacement of the etched surface, time step is controlled automatically to ensure a good stability of the surface profile. Langmuir adsorption and re-remission of radicals, spontaneous chemical etching and ion sputtering on both adsorbed and not adsorbed surface fraction are considered. The main difficulty to predict the etched surface features is the lack of the kinetic surface parameters. In this study, the etching kinetic parameters (sticking coefficient, etch coefficients on both adsorbed and no adsorbed surface fractions) of the InP surface are proposed by comparing the experimental and simulated etching rate curves as a function of the incident CH@sub 3@ flux. Least square optimization method is applied to deduce such estimated surface parameters. The simulation results show the effect of the plasma and surface kinetic parameters on the topography of the microscopic etched profiles.

PS-MoP10 Physical Characterization of the Etching of Low-k Hydrogen SilsesQuioxanes (HSQ) Dielectrics under Medium and High Density Plasma Conditions, ***C.H. Low***, *H. Cong, P. Yelehanka,* Chartered Semiconductor Manufacturing Limited, Singapore

The interconnect technology ventures into the development of low-k inter-metal dielectrics integration, arising from the need to reduce interconnect delay.@footnote 1@ The evolution of new low-k dielectric materials posts challenges to the conventional oxide etching processes.@footnote 2@ Hydrogen SilsesQuioxanes (HSQ)-based Flowable-Oxide (FOx), similar in composition as conventional oxide while offering low k values of 2.9 - 3.0, is used as the low-k IMD materials in our studies. The direct-on-metal (DOM) approach is employed for the integration of FOx as IMD layer for sub-0.25 micron application.@footnote 3,4@ The FOx layer is further capped with a thick PETEOS film, preventing it from degradation when subjected to subsequent high temperature processing steps. The etching of FOx integrated IMD stack is carried out using both TEL 85 DRM medium density plasma etcher and LAM TCP 9100 high density plasma etcher with different fluorocarbon etch chemistry. The physical characterization of the etching of FOx IMD stack under both conditions is demonstrated. In both cases, the FOx IMD vias are successfully opened with reasonably straight profiles. While high density plasma etching posesses in-situ PR strip capability for process simplification, it is also shown to induce more Si-H loss in the FOx layer. On the other hand, less damage is introduced to the FOx layer when etching under medium density plasma condition. Etch rate studies of FOx film cured at different temperature and duration as well as the film properties changes upon etching are also investigated. This is for better understanding of the etch process capability when subjected to different film curing conditions. @FootnoteText@ @footnote 1@L. Peters, Semicon. Int'l, p.64, Sep. 1998. @footnote 2@T.E.F.M. Standaert et.al., Mat. Res. Soc. Symp. Proc., p.265, vol.511, 1998. @footnote 3@B.T. Ahlburn et.al., Conf. Proc. ULSI XI, p.67, 1996. @footnote 4@Technical notes from Dow Corning Corp..

PS-MoP11 Modeling and Experimental Characterization of a Ti/Nitrogen/Ar Ionized Physical Vapor Deposition Tool, ***K. Tao***, *D. Mao, J. Hopwood,* Northeastern University

The deposition of adhesion layers, diffusion barriers, and seed layers into high-aspect-ratio features is a critical technology for next-generation integrated circuit interconnects. One method of directionally-depositing materials is ionized physical vapor deposition (IPVD). Sputtered atoms are ionized in IPVD by a high-density plasma and, subsequently, collimated toward the wafer by the plasma sheath potential. Although considerable work has been reported on the deposition of metal films using argon as the working gas, very little is known about reactive sputter deposition using IPVD. The formation of high quality metal-nitrides that exhibit high conformality is possible using a working gas of nitrogen and Ar. The Ti-Ar-N@sub 2@ plasma, for example, is used for the deposition of TiN. Reactive IPVD is being studied both experimentally and through analytical plasma modeling. The gas-phase densities of ionized, excited, and dissociated species of Ti, Ar, and nitrogen are predicted and compared with experimental measurements that include mass spectrometry, optical emission spectroscopy, and Langmuir probes. The dissociation of nitrogen is used to benchmark the model. Both the model and measurement show that the dissociation fraction lies between 5% and 20% and decreases with increasing plasma pressure. The effect of nitrogen on the degree of ionization of sputtered titanium, and therefore the bottom-coverage of high aspect ratio features, will also be discussed.

PS-MoP12 Influence of Dry Etching Gas Chemistry on the Formation of Line Edge Roughness of Patterned Oxide Hard Mask, ***A.S.-Y. Li***, State University of New York at Albany

As the pattern feature size shrinks to sub-quarter micron, line edge roughness (LER) of hard mask becomes critical in line-width control for pattern transfer. The patterns with LER affect both device characteristics and electrical properties. Contributions to LER of resist have been carefully studied. However, understanding of dependence of LER on dry etching gas chemistry is still in the very early stage. LER of oxide hard mask has been observed after being patterned with deep UV (DUV) resist on a magnetically enhanced reactive ion etching tool, even though no LER was seen on DUV resist before hard mask patterning. Results show that the roughness depends very much on etching gas chemistry. Introduction of O@sub 2@ into process will cause very serious edge roughness, while CF@sub 4@ gas can reduce its formation on the line edge. Experiments

also show that LER is first formed on the side wall of the resist and bottom anti-reflective coating layer, then it is transferred onto hard mask. Extending etching time will increase LER. Different etching behavior of gas chemistry has also been observed on resist. Top-view from critical dimension scanning electron microscopy shows a rough surface formed on resist after being etched using plasma containing either O@sub 2@ or Ar, but a much rougher surface has been seen on that from O@sub 2@ plasma. On the other hand, a combination of both Ar and O@sub 2@ plasma produces a very unform and smooth resist surface. Different etching behavior of gas chemistry, O@sub 2@, Ar, and CF@sub 4@ in hard mask opening is very helpful for us to understand the formation of the line edge roughness.

PS-MoP13 The Effect of Electrode Gap on CF@sub 2@ Distribution and Electrical Parameters in Fluorocarbon Plasmas, ***K.L. Steffens,*** *M.A. Sobolewski,* National Institute of Standards and Technology

Fluorocarbon plasmas are widely used by the semiconductor industry for etching and in situ cleaning of PECVD chambers. Previous studies in parallel-plate reactors have indicated that reactive species density distributions, precursor destruction efficiencies, plasma optical emission, and cleaning rates are correlated to the rf current measured at the upper, grounded electrode, I@sub ge@. In these studies, I@sub ge@ varied with changing pressure or was directly controlled by adjusting the impedance between the upper electrode and ground. The electrode gap is an additional parameter which can be varied to optimize the performance of these plasmas. In this study, performed on O@sub 2@/CF@sub 4@ chamber-cleaning plasmas in the capacitively-coupled Gaseous Electronics Conference Reference Cell, we investigated the correlations between electrode gap, electrical parameters, and the spatial distribution of the reactive CF@sub 2@ radical. Electrode gaps ranging from 0.5 cm to 2.25 cm were studied at pressures from 0.1 to 1.0 Torr. The 2-D density distribution of the reactive CF@sub 2@ radical was measured by planar laser-induced fluorescence (PLIF), and the regions where reactive species were generated were determined using spatially-resolved, broadband optical emission. The axial and radial uniformity and intensity of the emission and the CF@sub 2@ PLIF depended on both pressure and gap. The pressure at which the maximum radial uniformity in the CF@sub 2@ PLIF was observed correlated well with the maximum in I@sub ge@ but not with the minimum in plasma impedance. Measurements of rf current at the grounded electrode could be used to optimize the spatial distribution of reactive chemical species in reactors with differing electrode gaps, aiding in the optimization of chamber-cleaning plasmas and other fluorocarbon plasmas.

PS-MoP14 CF@sub x@ Radical and Etch Product Concentrations in Fluorocarbon Plasmas from Tunable Infrared Diode Laser Spectroscopy, ***Y. Men,*** University of Wisconsin, Madison, U.S.A*; I.C. Abraham, R.C. Woods,* University of Wisconsin, Madison

A sensitive diode laser spectrometer using multi-pass Herriot cells was employed in both an ECR etcher (30 passes with approximately 30 cm plasma depth) and in a 10 cm diameter, 1 m long hollow cathode DC discharge (46 passes). An IR diode laser operating near 1260 cm@super -1@ was used to study the CF@sub x@ (x = 1,2,3) radicals. Both CF and CF@sub 2@ were easily identified in a CF@sub 3@H ECR plasma, and their absolute concentrations were determined. Other fluorocarbon plasmas, e.g., C@sub 2@F@sub 6@ and C@sub 4@F@sub 8@, have also been investigated. The CF@sub x@ radical concentration dependences on plasma parameters, e.g., input power and neutral pressure, and on the partial pressure of added gases have been studied. To simulate actual etching conditions, radical concentrations over different wafer surfaces and at various bias powers have been measured. The CF@sub x@ concentrations with different reactant gases in the ECR etcher have been compared to those in the hollow cathode discharge. A diode laser operating in the 800-900 cm@super -1@ region is being used for similar investigations of SiF@sub x@ etch products.

PS-MoP15 Comparison of Plasma Density Measurements in ICP and Helicon Discharges using Langmuir probe, Plasma Oscillation Probe and Interferometry Techniques, *W. Zawalski,* Hiden Analytical Ltd.*;* ***J.D. Evans,*** University of California, Los Angeles

A comparison study of the application of various probe theories, including the so-called orbital motion limited@footnote 1@ and ABR@footnote 2@ theories, in the interpretation of Langmuir probe I-V characteristics is performed. Experimental data for the comparison is obtained in both an inductively coupled plasma (ICP) and a low-field helicon plasma source (HPS), over a wide range of parameters of interest to the plasma processing community.@footnote 3@ Measurements of N@sub e@ and N@sub i@ from the Hiden Electrostatic Plasma Probe (ESP) characteristics and ESPion software are compared to "known" values of N@sub e@ obtained via microwave interferometry and the plasma oscillation probe (POP) technique,@footnote 4,5@ in regimes including those where the probe theories yield different results. Closely spaced multiple peaks in the spectra of the POP are observed in some cases at higher RF input powers, possibly due to RF modulation of the source plasma density, leading to experimental uncertainty in N@sub e@ values thus obtained. Broadband low frequency electrostatic emissions and substantial peak broadening are observed when the beam-plasma instability excited by the probe is overdriven into the nonlinear regime. Other considerations for the applicability of the POP method will also be discussed. @FootnoteText@ @footnote 1@ J.G. Laframboise, Univ. Toronto Inst. Aerospace Studies Rept. 100 (1966). @footnote 2@ J.E. Allen, R.L.F. Boyd, and P. Reynolds, Proc. Phys. Soc. B 70, 297 (1957). @footnote 3@ N@sub p@ ~ 10@super 1@@super 0@-10@super 1@@super 2@ cm@super -@@super 3@, T@sub e@ ~ 2-4 eV, P@sub r@@sub f@ ~ 1 kW, P@sub o@ ~ 1-10 mTorr. @footnote 4@ T. Shirakawa and H. Sugai, Japan. J. Appl. Phys. 32, 5129 (1993). @footnote 5@ A. Schwabedissen et al., Plasma Sources Sci. Technol. 7, 119 (1998).

PS-MoP16 The Characteristics of PZT Thin Film by Dry Etching as a Variation of Substrate Temperature, ***T.H. An,*** *C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

The Lead Zirconate Titanate PbZr@sub x@Ti@sub 1-x@O@sub 3@ (PZT) ferroelectric thin films have received a great attention for the application on nonvolatile memory, Infrared sensor, electro-optical device and microelectromechnical system device etc. In order to accomplish the integration of these device, the etching process for both PZT film and electrode material must be developed. In particular, much research of PZT ferroelectric films as a dielectric material for storage capacitors of highly integrated memory devices has been carried out since this films have a high dielectric constant and remanent polarization. However, there has been little study regarding the etching mechanisms of PZT material as a function of substrate temperature. Dry etching of PZT thin film was studied to examine the etching characteristics as a variations of substrate temperature. PZT films were deposited on Pt/Ti/SiO@sub 2@/Si substrates by sol-gel process. PZT thin films were etched with Cl@sub 2@/BCl@sub 3@/Ar gas combination in an inductively coupled plasma (ICP) by varying substrate temperature. Etching properties were investigated in terms of etch rate, etch selectivity, etch damage. To understand etching mechanism, Langmuir probe and Optical emission spectroscopy (OES) analysis were utilized for plasma diagnostic, also X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and secondary ion mass spectrometry (SIMS) analysis for film composition were utilized.

PS-MoP17 The Roles of N@sub 2@ Gas in Etching of Platinum by Inductively Coupled Ar/Cl@sub 2@/N@sub 2@ Plasmas, ***J.H. Ryu,*** *N.H. Kim, C.I. Kim, E.G. Chang,* Chung-Ang University, Korea

Recently, much efforts has been expected on etching of platinum film, which is the candidate of electrode material in the capacitor structure for future DRAM and ferroelectric RAM (FRAM). One of the most critical problem in etching of platinum was generally known that the etch slope was gradual. Therefore, the addition of N@sub 2@ gas to the Ar/Cl@sub 2@ gas mixture, which has been proposed the optimized etching gas combination for etching of platinum in our previous article,@footnote 1@, was performed. The selectivity of platinum film to oxide as an etch mask was increased with the addition of N@sub 2@ gas, and the steeper etch slope could be obtained. We interpreted these phenomena as the results of the blocking layer on the oxide mask shaped N-O and Si-N. And it was confirmed by TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy) analysis. Moreover, it could be obtained the higher etch rate of platinum film. It was inspected that the more volatile compounds formed Pt-N were produced and the ion bombardment effects was increased. QMS (quadrupole mass spectrometry) and Langmuir probe were employed for each confirmation. @FootnoteText@ @footnote 1@ K. H. Kwon, C. I. Kim, S. J. Yun and G. Y. Yeom. "The Etching Properties of Pt Thin Films by Inductively Coupled Plasma", J. Vac. Sci. Technol. A 16(5), pp. 2772-2776, 1998.

PS-MoP18 Neutral Depletion and Transport Mechanisms in Large-Area High Density Plasma Sources, ***S.M. Yun,*** *K. Taylor, G.R. Tynan,* University of California, San Diego

Plasma uniformity has been recognized as a significant parameter in large sized high density plasma processing tools. In this paper we show

experimental and modeling results which indicate that significant neutral uniformity variations can also occur in high density plasma processing tools. The experiments are carried out in both inductively coupled plasma (ICP) and helicon plasma sources. The spatial distribution of reactive neutrals is measured using spatially resolved optical emission spectroscopy combined with Langmuir probe measurements of plasma density. The degree of on-axis neutral depletion is found to be determined by plasma density, neutral fill pressure, and neutral dissociation fraction. The observations can be explained by the "plasma pumping" effect, wherein electron impact ionization of neutral particles is followed by their rapid removal from the plasma by the presheath electric field. A one-dimensional neutral diffusion model that incorporates this mechanism provides reasonable agreement with our results. This net loss of neutral particles can result in a large (~50%) neutral density variation across 300mm wafers. The importance of neutral-surface interactions (i.e. the wall or wafer can be an effective source or sink of neutrals) is also examined.

PS-MoP19 The Study on The Method of Plasma-Generated-Polymer Attachment to PR Side Wall for Forming Smaller Contact Hole, ***K.I. Seo,*** *J.S. Hwang, U.I. Chung, K.W. Kang, M.-Y. Lee,* Samsung Electronic Co.Ltd., Korea

Resent PR (Photo Resist) patterning limit by KrF Deep UV (Ultra Violet) source is about 0.25~0.27µmm for contact pattern and 0.20~0.22µmm for line & space pattern. For patterning more small pattern size, line & space, new light sources such as ArF, X-ray, E-beam are being tested. But they are not adapted in mass fabrication yet. In this experiment, in order to overcome the patterning limit of photo process, we developed polymer attachment process to PR side wall for forming 0.15µmm size small contact. We tried to attach a uniform layer of polymer to PR side wall by generating various polymers in various gas plasmas such as CF@sub 4@/CHF@sub 3@/Ar, He/HBr, Cl@sub 2@/HBr. We found that C-Cl@sub x@-Br@sub y@ polymer, which has masking ability in the oxide etch process, was attached to PR side wall effectively in Cl@sub 2@/HBr gas plasma of the RIE (Reactive Ion Etching) type etcher which had a relatively high process pressure and a low density plasma. Based on the XPS (X-ray Photon Spectroscopy) result, the shape of the polymer attached PR, the dependency of the amount of the attached polymer on the contact size and the fact that polymer attachment process required PR loss, we proposed the mechanism of the polymer attachment process. It was observed the oxide etch rate was enhanced about 30% in contact hole size of 0.30µmm, and RIE-Lag was reduced in contact size range of 0.25~0.50µmm after the polymer attachment process, which needs further studies. We applied polymer attachment process to a real MDL (Merged DRAM with Logic) device, and obtained contact size of 0.15µmm by SEM (Scanning Electron Microscopy) measurement which was smaller than the contact size of normal process by approximately 50 nm as well as good size uniformity (@<=@ 20 nm), good particle (@<=@ 10 ea in entire wafer), uniform contact resistance in the range of 4800~5700@Ohm@/Cnt, and proper yield data.

PS-MoP20 Etching Mechanism of (Ba,Sr)TiO@sub 3@ Films in High Density Cl@sub 2@/BCl@sub 3@/Ar Plasma, ***S.B. Kim,*** Chung-Ang University, Korea*; Y.H. Lee,* Sung-Kyun-Kwan University, S.Korea, Korea*; G.Y. Yeom,* Sung-Kyun-Kwan University, Korea*; T.H. Kim,* Yeojoo Institute Technology, Korea*; K.H. Kwon,* Hanseo University, Korea*; C.I. Kim,* Chung-Ang University, Korea

(Ba,Sr)TiO@sub 3@ thin films have attracted great interest as new dielectric materials of capacitors for ultra-large-scale integrated dynamic random access memories (ULSI-DRAMs) such as 256 Mbit or 1 Gbit. In this study, Cl@sub 2@/BCl@sub 3@/Ar inductively coupled plasmas was used to etch (Ba,Sr)TiO@sub 3@ and the effect of etch parameter such as gas mixing ratio, coil rf power, dc bias voltage and chamber pressure. The characteristics of the plasmas were estimated using a Langmuir probe and optical emission spectroscopy (OES). (Ba,Sr)TiO@sub 3@ was etched under (Cl@sub 2@+BCl@sub 3@)/((Cl@sub 2@+BCl@sub 3@)+Ar) of 0.2. The maximum etch rate of the BST films was 56 nm/min under Cl@sub 2@/(Cl@sub 2@+Ar) of 0.2@super 1@, therefore Ar gas was constant at 0.2 and the ratio of Cl@sub 2@/BCl@sub 3@ was changed. The change of Cl, B radical density measured by OES as a function of BCl@sub 3@ percentage in Cl@sub 2@/BCl@sub 3@. The profile of (Ba,Sr)TiO@sub 3@ and residue remaining after the etch was investigated by scanning electron microscopy (SEM). To study on chemical reaction between BST and CF@sub 4@ and analysis composition of surface residue remaining after the etch, films etched with different Cl@sub 2@/BCl@sub 3@ gas mixing ratio were investigated using x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometer (SIMS). @FootnoteText@ ACKNOWLEDGMENTS This work was supported by GRANT No. KOSEF 981-0908-032-2 from the Korea Science and Engineering Foundation. 1. S. B. Kim, C. I. Kim, E. G. Chang, G. Y. Yeom, "Study on surface reaction of (Ba,Sr)TiO@sub 3@ thin Films by high density plasma etching", J. Vac. Sci. Technol. A Jul/Aug. (1999) will be published.

PS-MoP21 Short Time Scale Instabilities of Ion Energies in an RF driven Fluorocarbon-Plasma, ***G.J. Peter,*** *N. Müller, H. Zogg, H. Oehre,* Balzers Instruments, Principality of Liechtenstein

Fluorocarbon gases are widely used for etching in the semiconductor manufacturing. Besides the desired etching, especially C@sub 4@F@sub 8@ tends to polymerisation and to a build-up of insulating coatings in the plasma chamber. The energy distributions of various ions from an RF-driven C@sub 4@F@sub 8@ -Plasma were investigated by a PPM (Plasma Process Monitor) to determine the influence of such coatings on the ion energy distribution. The PPM is a combination of a differentially pumped quadrupole mass filter and an energy analyser. An energy resolution of 0.3 eV and unit mass resolution over the whole mass range are achieved. The only part of the PPM exposed to the plasma is kept on floating potential so that coating here can not change the electrical potential. The maximum energy of the ions scattered out of the main discharge increased from initially 20 eV to 75 eV during the processing time of a single wafer (less than one minute). The energy rise was reproducible over several cycles. The initial energy was reached again after cleaning in a pure Argon plasma when a low content of C@sub 4@F@sub 8@ in Argon was used as sputter gas. So the effect can be attributed to the coating of the walls and electrodes. When pure C@sub 4@F@sub 8@ was used the coating was thus intense that it could not be removed by sputter cleaning any more. Electrical probes were tested to measure the shift of the plasma (sheet) potential, however they failed after a few minutes because they got coated. The results achieved show the usefulness of a mass spectrometer based plasma monitor whenever the ion energy is a critical process parameter. Applications are in basic plasma research as well as in pilot production plants.

PS-MoP22 Influence of Electode-size and Finite Rise Time Effects on Plasma Sheath Expansion, ***G.-H. Kim,*** Hanyang University, Korea*; H.-S. Uhm,* Ajou University, Korea*; S.-Y. Rhee, Y.-W. Kim,* Hanyang University, Korea*; S.-H. Han,* KIST, Korea*; M.-P. Hong,* Samsung Electronics, Korea

Influence of the electrode-size effects on plasma sheath expansion is investigated for a negative voltage (Vo) at the thin, flat, conducting, circular disk of radius (R). Properties of the ion sheath expansion in plasma are also investigated for a target voltage with a finite rise time. Results show that the sheath expansion is proportional to the square root of time at the beginning and is proportional to the five-sixth power of time later on. The propagation of the sheath front is proportional to the one-third power of the combination, 2VoR/pi. Experimental measurements have been carried out and the measured data are compared with the newly developed theoretical results. Those results agree remarkably well.

PS-MoP24 Diode Laser Spectroscopy of C@sub 2@F@sub 6@ Discharges in a GEC Reference Cell, ***M.J. Barela,*** *K.S. Waters, H.M. Anderson,* University of New Mexico

Diode laser absorption spectroscopy (DLAS), optical emission spectroscopy (OES) and Langmuir probe measurements were used to characterize an inductively coupled GEC Reference Cell as a function of reactor source power, bias power, pressure and heated silicon ring temperature while etching patterned oxide wafers. These measurements are used to construct response surface models of the tool's plasma chemistry behavior versus oxide and photoresist etch rate behavior. The oxide and photoresist etch rate behavior was found to also be profoundly influenced by the temperature of the cooling wafer chuck, so this became a fifth variable in the study. In a C@sub 2@F@sub 6@ discharge, CF and CF@sub 2@ radical concentrations measured by DLAS were also found to be highly dependent on wafer chuck temperature. In a 6 mTorr C@sub 2@F@sub 6@ discharge at 350 W source power and 75 W bias power, typical CF and CF@sub 2@ concentrations were in the range of 1x10@super12@ cm@super -3@ and 3x10@super 13@ cm@super -3@ range. However, if the wafer temperature is allowed to rise toward 100 C, the CF@sub 2@ concentration increases dramatically apparently due to greater photoresist interaction with the plasma. If the wafer is properly cooled, the oxide and photoresist etch rates appear to be dominated by bias power and at low bias power, net deposition of fluorocarbon polymer prevails over net etching. However, with increased wafer temperature, both power and bias exert a strong influence on film etch rates and etching occurs at even zero applied bias power. The data is expected to provide an important database

for models of oxide etching in inductively coupled plasma tools. This project was funded by SEMATECH.

PS-MoP25 Silicon Oxidation-Depth Enhancement Employing Negative Ion under Transformer Coupled RF Bias, ***H. Shindo,*** Tokai University, Japan

Low temperature and low damage silicon oxidation technique is highly required in various ULSI processes. Especially for trench isolation of memory cell, the oxidation should be ion-assisted for directionality but with low damage. For this purpose, a method of negative ion assisted silicon oxidation was experimentally studied employing a microwave O2 plasma. A feasibility of high rate silicon oxidation with low damage at low temperature by negative ion was examined.In particular, effects of transformer coupled RF bias was deeply studied at various frequencies. The plasma produced in a 6 inch stainless-steel chamber was employed and the downstream plasma was mainly concerned because the negative ion was highly populated.Ion mass and energy analysis showed that the dominant negative ion was O- and its density was more than one order higher than O2-. The RF bias was applied with a transformer couple in combination with a DC voltage to irradiate the negative ion or positive one separately. The frequency of RF bias was varied from 40 kHz to 13.56 MHz. The oxidation depth showed a strong dependence on RF bias frequency, and its maximum was obtained at around 1 MHz, close to the negative ion plasma frequency.Thus it was concluded that the oxidation was due to the negative ions.The oxidation rate at the negative ion irradiation showed as high as 50 A/min at Vpp=65 V and it was five times higher than that at the positive ion irradiation of the same energy.This high rate of oxidation by the negative ion is due to its high chemical reactivity. An XPS analysis showed that in the film formed by the negative ion there was less suboxide compared with that by positive ion.

PS-MoP26 Deceleration of Silicon Etch Rate at High Aspect Ratios, ***J. Kiihamäki,*** VTT Electronics, Finland

The molecular flow conductance of a high aspect ratio feature can limit the etching species arriving at the bottom of the feature and thus limit the etch rate. Use of simple conductance model to predict etch rate of pulsed inductively couple plasma etch process gives good results when applied to linewidths typical in microelectromechanical systems (MEMS) at moderate aspect ratios, but at very high aspect ratio the conductance model does not predict the observed almost complete etch stopping. Other mechanisms are needed to explain it. In this paper the reasons of etch stop at the bottom of deep features are discussed. Measurement results of deep silicon etching are presented. Very deep holes of 30 and 60 µm diameter are etched into 1.3 mm thick silicon wafers to study the effect of process parameters. At moderate aspect ratios the bottom of the hole is nearly flat and side-walls are nearly vertical. At high aspect ratio the side-walls start to bow and the feature bottom turns into sharp spear head like. After long etch time the passivation breaks down near the top of the feature. The shape of the feature can have impact on step-coverage of passivation layer deposition during passivation step and passivation removal during etch step, which can cause the excessive sidewall etching and reduced etch rate at the feature bottom. Simple Monte Carlo calculation results of the effects of non-zero sidewall reaction probability and flow conductance of tapered tubes are presented. Main reason for etch stopping seem to be the loss of etchant species due to sidewall reactions.

PS-MoP28 Atomistic Simulations of Radical-Surface Interactions during Plasma-Enhanced Chemical Vapor Deposition of Si Films from Silane/Hydrogen Discharges, *S. Ramalingam, E.S. Aydil,* ***D. Maroudas,*** University of California, Santa Barbara*; S.P. Walch,* NASA Ames Research Center

Hydrogenated amorphous silicon (a-Si:H) films grown by deposition through silane-containing plasmas are widely used in solar cells and thin film transistors for flat panel displays. We present a study of the interactions of reactive radicals originating in the plasma with Si surfaces during plasma deposition from SiH@sub 4@/H@sub 2@ discharges based on recently developed classical force fields and ab initio calculations within density functional theory. Our simulation study employs a hierarchical approach that combines molecular-dynamics (MD) simulations for reaction identification and mechanistic understanding aided by molecular-statics and Monte Carlo simulations for reaction analysis. Interactions with isolated radicals during the initial stage of growth for each surface at submonolayer coverage are studied in detail to determine the surface chemical reactivity and the implications for the deposited film properties. The adsorption sites for the SiH@sub x@ (x=1,2,3) radicals are identified on the pristine and H-terminated Si(001)-(2X1) surfaces: the energetics of adsorption determined by the classical potential agree well with ab initio calculations. In addition, ultra-fast rate deposition of a-Si:H from each of the SiH@sub x@ radicals has been simulated through MD by repeatedly impinging the corresponding radical onto H-terminated Si(001)-(2X1) surfaces. SiH@sub 3@ radicals can abstract H atoms from the surface through an Eley-Rideal mechanism and return to the gas phase as silane molecules. Silyl radicals also can attach dissociatively onto the H-terminated Si surface at the dimer bond center. This insertion reaction leads to breaking of the dimer bond and subsequent transfer of a H atom from the radical to one of the dimer atoms resulting in the formation of two surface dihydride species. The energetics of this reaction is analyzed in detail both with classical and ab initio calculations. The theoretical results are compared with experimental observations.

PS-MoP29 Hydrogen Desorption from Acid Attacked Titanium after DC Glow-discharge Treatment, ***B.-O. Aronsson,*** University of Geneva, Switzerland*; B. Hjorvarsson,* Royal Institute of Technology, Sweden*; P. Descouts,* University of Geneva, Switzerland

Thermal desorption (TD) of hydrogen (H) from an acid attacked titanium (Ti) surface has previously@footnote 1@ been shown to depend on the presence of a surface oxide. The oxide was removed from Ti surfaces by using a DC glow-discharge (Ar plasma) treatment, and the subsequent change in the TD of absorbed H was studied. Biocompatibility is influenced by both surface chemical and topographical properties. In this study, the surface roughness of c.p. Ti samples was increased by at least a factor of 50 as measured by AFM.@footnote 1@ However, beside topographical modifications, acid attack also gives a dissolution of atomic H into the Ti sub-surface region and bulk which may result in a modification of the mechanical properties. Earlier work showed that TD above 400°C, where the oxide decomposes, is needed for H desorption.@footnote 1@ At these temperatures the morphology and mechanical properties of the Ti bulk are also modified and a lowering of the desorption temperature is desired. After plasma treatment the TD started below 300°C and the desorption activation energy was decreased from ca 2.0 (±0.3) to 0.8 (±0.2) eV/molecule. Ar plasma treatment was found to be efficient for a homogeneous sputter cleaning (characterized with AES), even of surfaces with a high surface roughness, and the native oxide was removed. The total amount of thermally desorbed hydrogen was inversely related to the plasma treatment intensity, while NRA profiles showed a complete elimination of the subsurface hydrogen after a medium intensity plasma treatment. AFM and SEM were used to characterize the topographical modification of plasma treated surfaces.@footnote 2@ @FootnoteText@ (1) Taborelli, M., et.al., Clinical Oral Implants Research, 1997, 8, 208-216 (2) Support from the ITI Foundation for the promotion of oral implantology, Switzerland, and from the Swiss National Fund, are greatly acknowledged.

PS-MoP31 Investigation of the TEOS Dissociation Coefficient by Electron Impact, ***C. Vallee,*** *A. Rhallabi, A. Granier, A. Goullet, G. Turban,* University of Nantes, France

Although O@sub 2@/tetraethoxysilane (TEOS) PECVD has been extensively used to deposit SiO@sub 2@-like films, the dissociation cross section of TEOS by electron impact is still unknown. In fact, most of the effort has been devoted to the determination of the TEOS fragmentation by O atoms (ko) since it is generally assumed that oxygen atoms are responsible for the dissociation of TEOS. Nevertheless, thanks to the experimental results obtained in a helicon reactor, it was suggested that TEOS fragmentation in a low pressure O@sub 2@/TEOS plasma was mainly achieved by electron impact while the main role of oxygen atoms was the etching of the organic part of the growing film. To get better insight into the TEOS dissociation by electron impact, we tried to determine the TEOS dissociation coefficient ke in a rf helicon reactor by developing a simple model which describes the experimental evolution of the growth rate with the distance from the TEOS injection. In this experiment, the TEOS gas is introduced at a point of the wall reactor instead of using a dispersal ring. A radial evolution of the deposition rate is obtained which can be related to a radial consumption of the TEOS. The model which gives ke at 3 eV (2 mTorr), is based on the following assumption: i) the deposition rate is proportional to the flux of fragments coming from the TEOS fragmentation by electron and oxygen atoms; ii) the spatial variation of the TEOS concentration is determined using a one-dimensional chemistry model. The first hypothesis requires the use of a sticking coefficient s. Dependence of ke with the value of s introduced in the model is also investigated. Finally, we found ke to vary from a few 10@super -8@ cm@super 3@s@super -1@ to a few 10@super -7@ cm@super 3@s@super -1@.

PS-MoP32 Electron Energy Control in Inductively Coupled Plasma Employing Multi-Mode Antenna, *H. Shindo,* ***T. Urayama,*** Tokai University, Japan

In the deep sub-micron etching for ultra large-scale-integrated circuit(ULSI) processes, numerous requirements of the plasma, such as high aspect ratio, high etching selectivity, are becoming increasingly critical. The requirements have promoted development of low-pressure and high density plasma. In these plasmas, however,the electron energy is prone to become too high at low pressures. In this work, a method of electron energy control was studied in an inductively coupled plasma by employing different azimuthal mode antenna. It is expected for electron energy to reduce at higher azimuthal mode antenna, because induction field is reversed with a shorter length. An inductively coupled plasma(ICP)was produced in a stainless-steel chamber of 350mm in diameter by supplying the RF power of l3.56MHz through the quartz window at one end. Langmuir probe diagnostics and optical emission spectroscopy were made through several vertical and horizontal ports of the chamber. The antenna is basically constructed with copper sheet of 0.3mm thickness, and the different azimuthal modes of m=0 and m=1 of one-loop antenna are realized by changing the feeder points of the RF current.The electron energy reduction was found in the m=1 mode by Langmuir probe measurement. This behavior was also confirmed by optical emission spectroscopy. The ArII lines became more intensive in the m=0 mode, while the ArI lines less intensive. The energy reduction in the m=0 mode was considered due to reverse of induction field with a shorter length in the higher mode antenna. The electron energy distribution function also showed less averaged energy in the m=1 mode.

PS-MoP33 Magnetized Inductively Coupled Plasma Etching of III-nitrides in Cl@sub 2@/BCl@sub 3@/O@sub 2@ and Cl@sub 2@/BCl@sub 3@/N@sub 2@, ***Y.H. Lee,*** SungKyunKwan University, Korea*; Y.J. Sung,* SungKyunKwan University, Korea, S.Korea*; G.Y. Yeom,* SungKyunKwan University, Korea*; J.W. Lee, T.I. Kim,* SAIT, Korea, South Korea

In this study, Cl@sub 2@/BCl@sub 3@/O@sub 2@ and Cl@sub 2@/BCl@sub 3@/N@sub 2@ inductively coupled plasmas were used to etch III-nitrides (GaN, AlN, and InN) and the effects of etch parameters such as gas combination and the effects of the magnets on the characteristics of the plasmas and etch properties of III-nitrides were investigated. The role of additive gases such as N@sub 2@ and O@sub 2@ to Cl@sub 2@/BCl@sub 3@ based plasmas to the etching of III-nitrides and the characteristics of plasma were estimated using a Langmuir probe, optical emission spectroscopy (OES), and quadrupole mass spectroscopy (QMS). Surface residue remaining after the etching was also investigated using x-ray photoelectron spectroscopy (XPS). The addition of O@sub 2@ and N@sub 2@ in Cl@sub 2@/BCl@sub 3@ generally increased III-nitrides etch rates for the small addition of O@sub 2@ and N@sub 2@ because more dissociated Cl radicals were generated by recombination processes (BO, B@sub 2@O, B@sub 2@O@sub 3@, and BN) between B from BCl@sub 3@ and O from O@sub 2@ or N from N@sub 2@. Using optical emission spectroscopy, radical peak intensities of BO, B@sub 2@O, B@sub 2@O@sub 3@, BN, and Cl intensity were estimated. The change of Cl radical density estimated by OES and QMS as a function of gas combination showed the same trend as the change of III-nitride etch rates, therefore, the etch rates of III-nitrides were related to the abundance of chlorine radical. Also, the use of magnets to the inductively coupled plasmas enhanced the etch rates of III-nitrides and improved the etch profile. We will show the effects of the magnets on the characteristics of the plasmas and the etch properties in more details at the presentation.

PS-MoP34 Grid Interactions with a High Density Plasma Source, ***J.E. Johannes,*** *T.J. Bartel,* Sandia National Laboratories*; C.K. Kim, D. Ecnomou,* University of Houston

Plasma interaction with a grid/screen is important in a number of applications. In neutral beam etching, for example, a grid is used to neutralize ions and generate collimated beams of energetic neutrals for anisotropic etch without charge damage. Neutron generators, used for neutron activation analysis in downhole logging, use a grid to define the Child-Langmuir surface where electrons are shielded, to extract an essentially pure ion beam for acceleration to a target. Finally, many ion sources and satellite thrusters are based on extraction of an ion beam from a plasma through a grid. The plasma conditions and the grid hole aspect ratio determine the neutral, ion, or plasma transport through the grid. Plasma-grid interactions are investigated for a range of plasma densities (1x1017-1x1019 #/m3) using particle based plasma simulation tools, and results are compared to experimental data. Icarus, a 2-D transient Direct Simulation Monte Carlo (DSMC) code and Mercury, a computationally fast, steady-state particle code are used to investigate the plasma behavior in front of and behind the grid. Electrons, ions and neutrals are treated as particles and an explicit Poisson solver, using the boundary element method, is used to compute electric fields. Simulations of both hydrogen and argon plasmas in an inductively coupled source were performed to generate boundary conditions for the grid. The grid hole diameter ranges from 30-1000 microns with a grid thickness of 250 microns. Simulation results are compared to measured ion fluxes and angular distributions collected over a range of grid hole aspect ratios. The optimal interaction parameters and hole aspect ratio required to minimize ion escape through the grid for neutral beam applications are discussed. Plasma-grid interaction calculations were also performed for higher density plasmas (1x1019 #/m3) typical of an arc discharge to investigate optimized hole aspect ratios for ion extraction for neutron generator applications.

PS-MoP35 Ultra-shallow n+/p and p+/n Junctions formed by Plasma Immersion Ion Implantation, ***J.D. Bernstein,*** *P.L. Kellerman, W. Krull, Yu. Erokhin, P. Frisella,* Eaton Corp.*; M.J. Rendon,* Motorola APRDL/Sematech

Plasma immersion ion implantation (PIII) is an emerging method being developed for shallow junction formation and other low energy, high dose ion implantation applications. The PIII process consists of placing a Si wafer in a plasma containing a desired dopant species and pulse-biasing the wafer to negative potentials in order to accelerate and implant dopant ions. In this work, BF@sub 3@, PH@sub 3@, and AsH@sub 3@ PIII are used for formation of ultra-shallow n+/p and p+/n junctions. As-implanted boron profiles produced from 2 to 10 kV BF@sub 3@ PIII are compared to those from mass-analyzed BF@sub 2@ implantation. The differences in the dopant profiles are attributed to the PIII ion energy distribution and the BF@sub 3@ plasma species composition. The relationship between sheet resistance and junction depth is investigated for PIII and mass-analyzed implants processed with a 1050 @super o@C spike anneal. Both n+/p and p+/n junctions produced by PIII meet S/D junction requirements of the National Technology Roadmap for Semiconductors (NTRS) for 70 nm CMOS devices.

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

Plasma-Surface Interactions I

Moderator: R.L. Jarecki, Sandia National Laboratories

8:20am **PS-TuM1 Probing Surface Layers during Inductively Coupled Plasma Etching using Laser-Thermal Desorption and Other Optical Techniques**, ***I.P. Herman***, *J.Y. Choe, N.C.M. Fuller,* Columbia University*; V.M. Donnelly, M.V. Malyshev, K.H.A. Bogart,* Bell Laboratories, Lucent Technologies **INVITED**

The etching of Si, Ge, and InP by an inductively coupled plasma (ICP) of chlorine is investigated by analyzing both the composition of the surface and the plasma during etching. The surface is probed by using laser-induced thermal desorption with an XeCl laser (308 nm) to desorb the steady-state adlayer and optical methods to detect these desorbed species. The development of a new method to detect optically these laser desorbed (LD) species is detailed, that of examining transient changes in the plasma-induced emission (PIE). This LD-PIE method is seen to be more universal than the previously reported detection by laser-induced fluorescence (LD-LIF), but is seen to require more calibration due to varying electron density and temperature with varying plasma conditions. This is detailed for Si etching, for which LD-PIE and LD-LIF results are compared. The calibration methods are seen to be valid when the surface is analyzed as the rf power supplied to the reactor is varied. A more complete picture of the etching process requires detailed characterization of the plasma through measurements of the constituents of the plasma. Neutral Cl@sub 2@ and Cl densities are determined by optical emission actinometry; Cl@sub 2@@super +@ and Cl@super +@ densities are determined by LIF and Langmuir probe measurements; and electron densities - needed for LD-PIE calibration - are measured by microwave interferometry. An improved understanding of the etching mechanism is obtained by combining the results of each of these measurements. This work was supported at Columbia by NSF Grant No. DMR-98-15846.

9:00am **PS-TuM3 Microscopic Uniformity in Oxide Etch during Overetch Time in Polysilicon Gate Etching**, ***K. Ono***, Kyoto University, Japan*; T. Mutumi,* Mitsubishi Electric Corporation, Japan

Plasma-surface interactions during polysilicon gate etching have been studied in ECR Cl@sub 2@ and Cl@sub 2@/O@sub 2@ plasmas, with emphasis on a better understanding of competitive mechanisms for microscopic uniformity i n etching of underlying SiO@sub 2@ that occur during overetch time. Experim ents were performed as a function of pressure, O@sub 2@ percentage, and rf b ias power, using samples for etching masked with a photoresist pattern of li nes and spaces (0.35-5 µm). The results of SiO@sub 2@ etching exhibit ed aspect-ratio dependent etch rates similar to those of poly-Si. In pure C l@sub 2@ plasmas, an RIE lag was observed at relatively low pressures (20%) was muc h larger for SiO@sub 2@ than for poly-Si. The inverse RIE lag also occurred at high pressures in pure Cl@sub 2@ plasmas, probably owing to background o xygen. Moreover, microscopically nonuniform thinning and breaking of thin g ate oxides was found to occur during overetch time; the thinning and breakin g occurred preferentially in large open fields in pure Cl@sub 2@ plasmas, wh ile in dense areas at high level O@sub 2@ addition in Cl@sub 2@/O@sub 2@ pla smas. A comparison of the experiments with the predictions of rate model an alysis indicated that the microscopic uniformity of SiO@sub 2@ etch rate pre sently observed in chlorine-containing plasmas is interpreted in terms of tw o competing processes caused by incoming ions and neutrals from the plasma i nto microstructures: carbon-enhanced oxide etching and removal of carbonaceo us materials by oxygen. The carbonaceous materials of interest are attribut able primarily to hydrocarbon fragments from sputtered photoresist, and the background and/or added oxygen is assumed to scavenge such hydrocarbon fragm ents adsorbed on SiO@sub 2@ surfaces before they enhance the oxide etch rate.

9:20am **PS-TuM4 Vacuum Beam Studies of Photoresist Etching Kinetics**, ***F. Greer***, *J.W. Coburn, D.B. Graves,* University of California, Berkeley

One factor limiting the development of reliable models of high density, low pressure oxide etch plasmas is the relatively poor understanding of the plasma-photoresist surface interactions. In particular, the relatively high rates of photoresist (PR) loss experienced in high density fluorocarbon plasmas is a significant problem. It has long been accepted that fluorine plays a key role in controlling the oxide to PR etch rate selectivity. The addition of hydrogen has been shown to improve this selectivity by scavenging fluorine from the tool. To develop reliable models of these etch tools, it is necessary to understand how this process occurs and to predict PR etch rates as a function of the neutral to ion flux ratio at the surface as well as the ion energy dependence. The neutral and ion compositions in practical etch systems are difficult to measure and control accurately; however, vacuum beam systems can probe the plasma-surface interactions of various samples by employing independent beams of both neutral and ionic species. The complicated chemistry of fluorocarbon plasmas is modeled with argon ions and independent neutral fluxes of hydrogen and fluorine atoms intersecting at the surface of a photoresist sample. We will present experimental evidence that the etch yield of photoresist (carbon atoms removed per incident argon ion) under these conditions is quite high compared to that of silicon and silicon dioxide. The presence of a simultaneous flux of hydrogen on the photoresist surface does not affect the etch yield measured despite the fact that HF does form during the etching process. In addition, the relative reactivity of hydrogen and fluorine atoms for abstraction of one another on the photoresist surface has been measured with modulated beam mass spectrometry with and without ion bombardment. These results are incorporated into a phenomenological model of the photoresist etching process.

9:40am **PS-TuM5 The Relationship of Etch Reaction and Reactive Species Flux in C@sub 4@F@sub 8@/Ar/O@sub 2@ Plasma for SiO@sub 2@ Selective Etching Over Si@sub 3@N@sub 4@**, ***M. Matsui***, *T. Tatsumi, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between reactive species flux and their inducing surface reaction layer was studied in a SiO@sub 2@/Si@sub 3@N@sub 4@ highly selective etch process. C@sub 4@F@sub 8@/Ar/O@sub 2@ plasma in a dual-frequency (27/0.8 MHz) parallel plate etch system was employed to etch the specimens that were quantatively analyzed by using X-ray photoelectron spectroscopy (XPS). CF@sub x@ radical flux was controlled by adjusting the C@SUB 4@F@SUB 8@ flow rate ratio. The influence of the O@SUB 2@ partial pressure was also investigated. Ion flux (6 x 10@super 16@ cm@super -2@s@super -1@) and the Vpp of bias rf (1450 V) were kept constant. We have found that the etch rates strongly depend on the fluorocarbon film thicknesses. Under higher Si@sub 3@N@sub 4@ etch rate conditions with low CF@sub 2@ flux or high O@sub 2@ partial pressure, the fluorocarbon film on the Si@sub 3@N@sub 4@ surfaces was thinner than film in a high-selectivity condition (5-6 nm). The oxidation of the Si@sub 3@N@sub 4@ surface was also observed. On the other hand, the fluorocarbon film thicknesses on the SiO@sub 2@ surface were less than 1 nm where the etch reaction proceeds on the SiO@sub 2@ surface. The fluorocarbon films on SiO@sub 2@ were thinner than films on Si@sub 3@N@sub 4@ at the same CF@sub x@-radical-flux. This difference of the film thickness is considered to be due to the outflux of oxygen from SiO@sub 2@, that can remove CF species from the SiO@sub 2@ surface. The fluorocarbon films on the SiO@sub 2@ are so thin that the ion energy is not reduced when passing through the films, while those on the Si@sub 3@N@sub 4@ are almost as thick as the ion range of 1450 V. In conclusion, highly selective etch is achieved in the condition where the minimum partial pressure of O@sub 2@ and proper amount of CF@sub x@ radical flux in order to control the fluorocarbon film thicknesses on Si@sub 3@N@sub 4@ and SiO@sub 2@. @FootnoteText@ This work was supported by NEDO.

10:20am **PS-TuM7 Anisotropic Etching of Polymer Films by High Energy (~ 100s of eV) Oxygen Atom Neutral Beams**, *S. Panda,* ***D.J. Economou***, University of Houston*; L. Chen,* Chen Laboratories

As microelectronic device dimensions continue to shrink, charging damage is becoming a major issue. Charging damage can result in anomalous etch profiles (notching) and reduced etch rate in high aspect ratio features (aspect ratio dependent etching), in addition to thin oxide breakdown. A way to minimize or eliminate charging damage is to use a neutral beam instead of reactive ion etching. High flux, controlled energy, and high directionality are critical requirements of such neutral beam. We have developed a neutral beam reactor that generates a collimated, high energy (30-300 eV), high flux (equivalent of several mA/cm2) neutral beam. An inductively coupled source is used to generate a high density plasma. Positive ions are extracted through a grid with high aspect ratio holes, which also serves to neutralize the ions. The neutral beam reactor was tested by etching a polymer film using an O-atom beam extracted from an oxygen plasma. High rate (~ 1 micron/min), microloading-free, high aspect ratio etching, with straight sidewalls was demonstrated. The plasma source and the region downstream of the gird were characterized by optical

emission actinometry and Langmuir probe measurements to shed light on the effect of source operating parameters (pressure, power, extraction voltage) on species densities and fluxes, and the degree of ion neutralization.

10:40am **PS-TuM8 X-ray Photoelectron Analysis of Sidewall Passivation Films formed during Sub 0.1 µm Silicon Gate Etch Processes**, ***L. Desvoivres***, France Telecom-CNET, France; *L. Vallier,* France Telecom-CNET and CNRS; *O. Joubert,* France Telecom-CNET and CNRS, France

As integrated circuits dimensions are rapidly scaling down to 0.1 µm regime and below, the critical dimension (CD) control of the etched features becomes more and more challenging. The critical dimension budget (10% of the nominal dimension) is usually shared between lithography and etching. Each individual step should be carefully optimized. For silicon gate applications, CD variations across the wafer are usually attributed to etch non-uniformities. However, the passivation layer which forms on the silicon sidewalls has also a direct impact on CD control since the passivation layer thickness is aspect ratio dependent. In the future, a careful control of the nature and thickness of this layer will become critical. In this work, we have investigated the impact of the chemistry (hydrogen bromine, chlorine with different oxygen dilutions) and of the plasma conditions on the formation of the sidewall passivation film. This study has been performed in a high density plasma Helicon source, operated at low pressure. The sidewall film has been analyzed using x-ray photoelectron spectroscopy. The sidewall passivation film formed in 125 nm L/S features is a 2 nm thick SiO@sub 2@ like film composed of oxygen, halogen and silicon. This film is mainly formed during the main etch step of the process thanks to etch products deposition on the sidewalls of the features. It gets oxidized at the very beginning of the overetch step thereby allowing halogen to be desorbed and the oxygen concentration to be increased. The impact of the plasma operating conditions and chemistry on the nature and thickness of the sidewall film will be presented. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

11:00am **PS-TuM9 Kinetic Roughening of GaAs (001) During Plasma Chemical Etching**, ***S.W. Robey***, National Institute of Standards and Technology

Kinetic roughening of the GaAs(001) surface during plasma etching by H and CH@sub 3@ radicals was investigated using atomic force microscopy in combination with RHEED and Auger spectroscopy. The evolution of the surface morphology was tracked as a function of etching time, temperature, and plasma composition. Large changes in the form of the surface roughness were observed and reflect variations in the surface dynamics which induce correlations from point-to-point on the surface. These changes involved not only the length scale of surface features, but also distinctive variations in the anisotropy between [110] and [-110], particularly as a function of surface temperature. Surface height data were analyzed to extract height correlation functions, which provided dynamic and roughness scaling exponents for comparison with theory. Measured height-difference correlation functions displayed two distinct roughness scaling regimes with a crossover that increased from ~ 30 nm to ~ 150 nm with increasing surface temperature between 500 K and 700 K. At short length scales, a roughness coefficient of ~ 0.7 was typically observed, while a logarithmic dependence was generally observed at larger length scales. Calculated height-correlation functions based on continuum models that include competition between short length-scale surface diffusion and long-range desorption dynamics reproduce this crossover behavior and offer the potential for extracting information on changing surface dynamics as a function of etch conditions.

11:20am **PS-TuM10 Measurements and Modeling of the Absolute Sputtering Yield of Nitrided and Non-nitrided Diffusion/Barrier Film Materials with Incident N+ and Ar+**, ***R. Ranjan***, *M.H. Hendricks, J.P. Allain, D.N. Ruzic,* University of Illinois, Urbana-Champaign

The angular distribution of sputtered material and the absolute sputtering yield of metal targets by argon ions at energies less than 1000 eV has been measured in previous work for a number of materials.@footnote 1@ The application of TiN and TaN films for both diffusion barrier and enhanced metallization properties has grown in the advent of copper metallization. The conformal nature of such diffusion barriers has been addressed with the advancement of IPVD magnetron sputtering systems. In order to understand the physical processes on magnetron targets used in such systems, an experiment in the Ion-surface InterAction Experiment (IIAX) facility has been designed to measure the absolute sputtering yield of nitrided and non-nitrided barrier/seed layer material targets with incident N and Ar ions. A Coultron ion source is used to create and accelerate gaseous ions onto a 100 mm@super 2@ metal target. The bombarding ions are mass-selected through an E X B filter and decelerated near the target. The target can be rotated in order to provide variation in the angle of incidence. A plasma cup is used to remove the first few monolayers and thus provide a "clean" surface. This method also provides for "nitriding" the layer on the target surface. A newly designed dual quartz crystal oscillator unit is rotated in front of the target to collect the sputtered flux measuring the absolute sputtering yield. Modeling is performed by VFTRIM3D, an enhanced version of TRIM, a Monte Carlo code which includes fractal geometry and a non-binary collision model.@footnote 2@ @FootnoteText@ @footnote 1@ P.C. Smith, D.N.Ruzic, submitted, J. Vac. Sci. Technol.A @footnote 2@ D.N.Ruzic, Nuclear Instrum. and Methods in Phys. Res. B47 (1990) pp.118-125

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

Plasma Diagnostics II

Moderator: M.G. Blain, Sandia National Laboratories

2:00pm **PS-TuA1 Infrared and Microwave Absorption Diagnostics of Plasmas for Silicon Oxide Etching and Deposition**, ***R.C. Woods***, University of Wisconsin, Madison **INVITED**

Absorption spectroscopic diagnostics are non-invasive and provide absolute species concentrations, integrated along the radiation path. Infrared diode laser spectroscopy uses molecular vibration-rotational lines, while microwave spectroscopy looks at pure rotational lines of molecules. The sensitivity of both is high, and their high resolution permits unambiguous separation and identification of many species. We have recently used IR diode laser spectroscopy to measure CF, CF@sub 2@, and CF@sub 3@ absolute concentrations in an inductively coupled GEC etching reactor in G. Hebner's laboratory at Sandia N.L. The three species' densities were studied as functions of power and pressure in C@sub 2@F@sub 6@ and CF@sub 3@H discharges, over both blanket silicon and blanket photoresist wafers. A home built microwave spectroscopic diagnostic has similarly been used at Wisconsin to study concentrations of several species in ECR plasmas intended for deposition of silicon oxide or fluorinated silicon oxide. Gas mixtures studied are silane/oxygen and TEOS/oxygen, or these with admixture of SiF@sub 4@. Species detected by this technique include SiO, CF@sub 2@, SiF@sub 2@, SiF@super +@, and several TEOS oxidation products, e.g., methyl and ethyl alcohol, formaldehyde and acetaldehyde, and formic acid. Although in principle these two absorption spectroscopic techniques are very closely related, sometimes looking at the same molecules and even absorbing from the same quantum levels, each has its own advantages and limitations, and these will be briefly discussed here. This work was supported by National Science Foundation Grant #EEC-8721545 and by SEMATECH under contract no. 38010430.

2:40pm **PS-TuA3 Thomson Scattering with Gated Intensified CCD Detectors for Diagnostic of rf Discharge Plasmas**, ***S.A. Moshkalyov***, *T. Morrow, C. Thompson, W. Graham,* Queen's University of Belfast, Northern Ireland, UK

Thomson scattering (TS) with high-repetition rate lasers has been recently introduced as a diagnostic of electron parameters (electron density and electron energy distribution function, EEDF) in low-temperature gas discharge plasmas. This method has some distinct advantages over other techniques (like electric probes) which are commonly used to measure electron parameters in gas discharges. This technique is non-intrusive, and the interpretation of data is straightforward. However, due to the small cross-section of light scattering by free electrons, TS signals are extremely low (~ 20-30 photoelectrons/pulse for an electron density of 10@super 11@ cm@super -3@). To improve signal-to-noise ratios, measurements are typically made by accumulating the signals over ~10@super 3@ laser pulses. In most TS experiments, single-channel photomultiplier tubes are used for the light detection. A further step in the diagnostic development is the use of multichannel detectors such as gated intensified CCD's which record the entire TS spectrum and thus reduce considerably the time needed for measurements of the electron parameters. In our experiments, TS system with 10 Hz YAG laser (0.5 J at 532 nm) and a low-noise ICCD detector is used for diagnostics of an inductively coupled RF discharge plasma in a GEC reference cell. Experiments were carried out in Ar plasma for low pressures (25-250 mTorr) and relatively low powers (30-70 W). Experiments have shown that high accuracy of EEDF measurements in an extended range of electron energies (up to 12-15 eV) can be achieved by accumulating TS signals in 500-2500 pulses, with overall measurement time as small as 2-10 minutes. For high argon pressures EEDF has shown to be close to Maxwellian, while for low pressures strong deviation from Maxwellian distribution has been observed. The study of the effect of other gases admixtures to Ar is now on the way.

3:00pm **PS-TuA4 Determination of Electron Temperatures and Species Concentrations During Aluminum Etching**, ***V.M. Donnelly***, *M.V. Malyshev, S.W. Downey, J.I. Colonell, N. Layadi,* Bell Laboratories, Lucent Technologies

Electron temperatures (T@sub e@) and species concentrations were obtained in chlorine-containing, high-density, inductively coupled plasmas (Applied Materials decoupled plasma source (DPS) metal etcher), using trace rare gases optical emission spectroscopy (TRG-OES). Measurements were carried out as a function of total pressure, source power, fraction of BCl@sub 3@ added to Cl@sub 2@ and substrate material (SiO@sub 2@, Al, and photoresist). A small amount (1.7% each) of all five rare gases was added to the plasma and emission spectra were recorded. TRG-OES T@sub e@ s corresponding to the high energy tail of the electron energy distribution function were derived from the best match between the observed and computed rare gas emission intensities. At source and bias powers of 1000 and 100 W, TRG-OES T@sub e@ s in Cl@sub 2@/BCl@sub 3@/N@sub 2@/rare gas plasmas increased from 1.5 eV at 40 mTorr to 3.0 eV at 3 mTorr, in good agreement with values computed from a global model and somewhat lower (at higher pressures) than those measured with a Langmuir probe. Surprisingly little dependence of T@sub e@ on substrate material was found. Reduced plasma induced damage at higher pressures correlated with a drop in both T@sub e@ and plasma density, but appears to be due mostly to the lower T@sub e@. Cl@sub 2@, Cl, BCl@sub 2@, BCl, B, AlCl@sub 2@, AlCl, Al, N@sub 2@ and BN emissions were identified. Qualitative, and in some cases quantitative absolute number densities were obtained by dividing these emission intensities by that from Ar, or Xe, corrected for electron impact excitation from Xe metastables.

3:20pm **PS-TuA5 Peter Mark Memorial Award Address**, ***E.S. Aydil***[1], University of California, Santa Barbara **INVITED**

4:00pm **PS-TuA7 Cavity Ring Down Spectroscopy for the Detection of Hydrocarbon Radicals during a-C:H Deposition**, ***K.G.Y. Letourneur***, *M.C.M. van de Sanden, R. Engeln, M.G.H. Boogaarts, D.C. Schram,* Eindhoven University of Technology, The Netherlands

Cavity Ring Down spectroscopy can be used in order to quantify the relative influence of radical species impinging on a growth surface. This enhanced absorption technique allows the determination of low species ground state densities as well as the evaluation of their rotational and vibrational temperature. It also allows for time and space resolved measurements. Cavity Ring Down spectroscopy has been applied during the deposition of hard hydrogenated amorphous carbon films obtained from a remote argon arc plasma in which acetylene is injected as carbon precursor. The C@sub 2@H@sub 2@ molecules are subsequently dissociated by argon ions and electrons, present in the plasma, producing hydrocarbon radicals (C@sub 2@H@super *@ and CH@super *@) responsible for deposition (rates up to 20 nm/s). However, hitherto, to the best of our knowledge, no direct detection of the ground state of those radicals has ever been reported in such environment. Detection of the ground state of the CH and C@sub 2@H radicals via CRD spectroscopy around 430 nm and 276 nm respectively are presented. Typical ground state densities of CH of around 10@super 17@ m@super -3@ are found. The results are used to develop a model for the deposition process of hydrogenated amorphous carbon from a remote plasma.

4:20pm **PS-TuA8 Characterization of Transformer Coupled Oxygen Plasmas by Trace Rare Gas-Optical Emission Spectroscopy and Langmuir Probe Analysis**, ***N.C.M. Fuller***, Bell Laboratories, Lucent Technologies and Columbia University; *M.V. Malyshev, V.M. Donnelly,* Bell Laboratories, Lucent Technologies; *I.P. Herman,* Columbia University

Trace rare gas-optical emission spectroscopy (TRG-OES) and Langmuir probe analysis have been used to measure the electron temperature, T@sub e@, in a high-density inductively (transformer) coupled (TCP) 10 mTorr oxygen plasma as a function of the 13.56 MHz radio frequency (rf) power. Rare gas actinometry and modeling at 7774 and 8446 Å have been used to determine the absolute densities of ground state atomic and molecular oxygen and the O(@super 1@D), O(@super 1@S) and O@sub 2@(a @super 1@@delta@@sub g@) metastables in the plasma. In the bright (inductive) mode, T@sub e@ increases from 2.7 to 3.4 eV for the electrons sampled by the Langmuir probe and from 4.1 to 5.5 eV for the high energy electrons sensed by TRG-OES, as rf power is increased from 100 to 1046 W. In the dim (capacitive) mode, below 45 W, T@sub e@ increases from a few eV at very low rf power to ~ 6 eV at 45 W. T@sub e@ decreases from 4.5 ± 1.5 eV at ~ 45 W to ~ 3.3 ± 0.8 eV at ~ 100 W. The gas dissociation peaks at ~ 40% at the maximum rf power density of 5.7 Wcm@super -2@ (1046 W), for which the ground state atomic and molecular oxygen concentrations are 2.5 x 10@super 14@ cm@super -3@ and 3.9 x 10@super 13@cm @super -3@ respectively. At this power density, the densities of O(@super 1@D) and O(@super 1@S) are 2.0 x 10@super 13@ cm-3 and 4.5 x10@super 11@ cm-3 respectively and the metastables collectively account for ~ 8% of all neutral species. For this

[1] **Peter Mark Memorial Award Winner**

power density, excitation of the metastables contribute ~ 44% and ~ 50% of the emission observed at 7774 and 8446 Å respectively, with the O(@super 1@D) metastable being the principal contributor. In the dim mode, the densities of O(@super 1@D) and O(@super 1@S) are three and five orders of magnitude smaller, respectively, than that of ground state atomic oxygen. Throughout the rf power range investigated, the density of O@sub 2@(a @super 1@@delta@@sub g@) is ~ one-third that of O(@super 1@D).

4:40pm **PS-TuA9 Diagnostics of Large-area Plasma Produced by Surface Waves on a Metal Wall with Periodicity**, ***T. Yamauchi***, *K. Aoki,* Toshiba Corporation, Japan; *H. Sugai,* Nagoya University, Japan

Surface-wave plasma is a promising next-generation plasma source since it readily yields a large-area high-density plasma at low pressures. In most cases, surface waves at 2.45GHz are excited along a dielectric wall, however, the use of a large-area dielectric wall often induces serious wall erosion and impurity release. To avoid such problems, the use of a metal wall with periodic structures which results in an increase in plasma density as well as an improvement in density uniformity is proposed in this paper. The top of the vacuum chamber consists of an Al plate(340mm diameter) comprising two quartz windows (20mm width) which also serve also serving as slot antennas. A periodic structure was installed on the Al plate. The experimental conditions are an Ar gas flow rate of 60sccm, a pressure from 30 to 70Pa and a microwave power of 2kW. We obtained the electron density of 10@super11@10@super12@cm@super-3@, which exceeds the cut off density (7.44 x10@super10@cm@super-3@)for 2.45GHz. The behavior of the ion saturation current, electron density and electric field intensity between two slots. Without the periodic structure the values show peaks under each slot antenna, thus indicating the influence of microwave radiation from the slot antennas themselves. Accordingly, it is revealed that the periodic structure on the metal wall is effective for generating a large-area surface-wave plasma.

5:00pm **PS-TuA10 UV Absorption Spectroscopy of Pulsed Fluorocarbon Plasmas**, ***B.A. Cruden***, *K.K. Gleason, H.H. Sawin,* Massachusetts Institute of Technology

Thin polytetrafluoroethylene(PTFE)-like films have been deposited in a pulsed capacitively coupled plasma from a variety of fluorocarbon precursors. It has been shown that pulsing of the plasma allows for composition control, giving reduced amounts of cross-linking and branching, and a higher CF@sub 2@ content. While some precursors, such as hexafluoropropylene oxide (HFPO), appear to deposit primarily in the off-time and is believed to be dominated by long-lived difluorocarbene species, other precursors, such as tetrafluoroethylene (TFE) show a linear dependence of deposition on duty cycle, suggesting deposition occurs primarily in the on-time period. To help elucidate the nature of the deposition processes and the differences between these precursors, UV absorption has been used to measure CF@sub 2@ concentrations quantitatively. In the plasmas examined here partial pressures of CF@sub 2@ are observed in the range of 5-15 mtorr for a 1 torr total pressure. Transients in concentration have been modelled by a elementary mole balance and effective reaction constants have been obtained. Optical emission spectroscopy and actinometry are also used to study the role of other species including O, F, CF and CF@sub 3@. XPS is used to study how the composition of the films varies with precursor and pulsing conditions, and can be related to the gas phase concentrations as measured by UV Absorption. Additionally, a quartz-crystal microbalance (QCM) has been used to measure deposition rates during the plasma on and off times.

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

Feature Profile Evolution

Moderator: J. Chang, University of California, Los Angeles

8:20am **PS-WeM1 The Ion-Assisted Etching and Profile Development of Silicon in Molecular and Atomic Chlorine**, ***E.S.G. Shaqfeh,*** Stanford University **INVITED**

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, was performed. 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, incorporating chlorine adsorption, atomic to molecular chlorine surface recombination, and the ion-induced desorption of adsorbed chlorine and silicon chloride products. 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 effects, where traditional lag was observed for features etched using an isotropically distributed background chlorine flux and inverse lag was observed for features etched with a molecular and atomic chlorine flux arriving directly from the effusive source. Microtrenching was also present in the etched features. 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. Using the simulation, 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 and were found to be in good agreement.

9:00am **PS-WeM3 Investigation through Simulation of the Effect of Ar Addition on the Cl@super +@/Cl@sub 2@@super +@ Ratio in Chlorine Discharges**, ***J. Helmsen,*** *P. Loewenhardt,* Applied Materials Inc.

.A cause of compromise in commercial Al etch processes that employ Cl discharges is the removal of Cu residue. This residue is due to the presence of Cu that has been added to the Al to prevent electromigration. Investigation of processes that successfully remove this residue have shown that the Cl@super +@/Cl@sub 2@@super +@ ratio measured near the wafer has been found to positively correlate with residue removal.@footnote 1@ This ratio can increase as a result of lower pressures and increased source powers, but also can increase due to the addition of Ar into the plasma. Investigation of the ratio through the use of simulation in pure Cl plasmas has shown the ratio is controlled by charge exchange between Cl@super +@ and Cl@sub 2@ producing Cl@sub 2@@super +@ and Cl.@footnote 2@ The proposed influence of Ar is dilution of Cl@sub 2@, thereby allowing a greater proportion of Cl@super +@ to not participate in the reaction and reach the surface. The effect is shown through the use of plasma simulation with the Hybrid Plasma Equipment Model (HPEM).@footnote 3@ @FootnoteText@ @footnote 1@ P. Loewenhardt, "Plasma Diagnostics: Use and Justification in an Industrial Environment", 51st Annual Gaseous Electronics Conference, Maui, Hawaii, Oct. 1998. @footnote 2@ J. Helmsen, D. Hammer, J. Yamartino and P. Loewenhardt, "Investigations of Rate Coefficients in the Cl Model", IEEE Transactions on Plasma Science (Accepted for Publication) @footnote 3@ P. L. G. Ventzek, M. Grapperhaus and M. J. Kushner, "Investigation of Electron Source and Ion Flux Uniformity Measurements in High Plasma Density Inductively Plasma Tools Using 2-Dimensional Modeling", J. Vac. Science Tech. B 12, 3118-3137 (1994)

9:20am **PS-WeM4 Does Mask Charging Influence Sidewall Trench Formation ?**, ***H.C. Lee,*** *G.S. Hwang,* California Institute of Technology*; H.S. Lee,* Hyundai Electronics Co. Ltd., Korea*; K.P. Giapis,* California Institute of Technology*; L. Desvoivres, L. Vallier, O. Joubert,* France Telecom-CNET, France

There has been some controversy in the etching community about how and to what extent charging effects influence profile evolution during the main etch in high-density plasmas. Microtrenching, for example, is believed to occur as a result of forward scatt ering of ions at the sidewalls. While charging is not essential for microtrenching, simulations have shown that mask charging could perturb the ion trajectories so that more ions scatter at the sidewalls; the resulting increase in scattered ion flux causes deeper microtrenches. This effect is difficult to prove when the mask is made of polymeric material because mask erosion influences the profile. Mask faceting, in particular, could increase the scattered ion flux to the trench bottom thereby dominating microtrench formation. It is then imperative that a hard mask be used to prevent any chemical or physical interference with trench profile evolution. We have performed a combined experimental and theoretical study of the contribution of mask charging to m icrotrenching. A Si wafer was patterned with gratings of hard oxide masks of linewidths down to 0.2 μm and then etched in a high-density, pure Cl@sub 2@ plasma to various depths. Three different mask thicknesses were tried: 0.2, 0.5, and 0.7 μm. Profile evolution simulations in the ion-limited regime predict that microtrenching should worsen with mask thickness because of increased scattering due to: 1) the larger sidewall area, and 2) ion deflection caused by upper mask sidewall charging. For mask aspect ratios larger than 3:1, charging of the lower part of the sidewall leads to an ion focusing effect that decreases significantly the microtrench depth resulting in rounded trench bottom profiles. While the experimental results generally support these trends, we find also important differences in the profile shapes. A side-by-side comparison will be shown and the charging contributions to microtrenching will be discussed.

9:40am **PS-WeM5 Modeling Feature Evolution in Plasma Processes**, ***D.B. Graves,*** University of California, Berkeley **INVITED**

Control of the shape of features during etching or deposition is central to the success of many plasma processes used for semiconductor manufacturing. Unfortunately, current models of feature shape evolution are relatively primitive with limited predictive capability. A major goal of plasma process modeling is to develop truly predictive feature shape evolution simulations. One reason for the difficulties experienced in developing predictive shape evolution models is that many parts of the plasma play a role. Events at the tool scale help to govern the composition, flux and energy of ionic and neutral species that impact substrates. The sheath and local presheath above the substrate play important roles in governing positive ion energy and angular distributions at surfaces. In some cases, electron energy distributions and negative ions can be important in feature differential charging phenomena. Features are themselves often complex, with materials and geometries that challenge current models. Processes within a feature, including neutral reaction, ion-sidewall scattering, sputtering, charge transport and redeposition of etch products are all potentially important. An important issue is the sensitivity of the predicted shape evolution to inaccuracies in various parts of the model. In this talk, I will review the progress in developing models of reactive plasma processes, focusing on the phenomena that are known or suspected to affect feature shape evolution. Predictive feature shape evolution models must include the tool scale, the sheath, the feature itself, as well as processes occurring at surfaces. I will review progress made in using vacuum beam experiments, atomistic simulations, and plasma experiments that focus on feature shape evolution. I will highlight the need for more systematic studies of plasma process feature shape evolution, the development of novel sensors, and the development of physically-based, phenomenological surface rate expressions.

10:20am **PS-WeM7 Feature Profile Evolution of SiO@sub 2@ Trenches in Fluorocarbon Plasmas**, ***H.H. Hwang,*** Thermosciences Institute*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center*; V. Arunachalam, S. Rauf, D.G. Coronell,* Motorola

Etching of silicon microstructures for semiconductor manufacturing in chlorine plasmas has been well characterized. The etching proceeds in a two-part process, where the chlorine neutrals passivate the Si surface and then the ions etch away SiCl@sub x@. However, etching in more complicated gas mixtures and materials, such as etching of SiO@sub 2@ in Ar/C@sub 4@F@sub 8@, requires knowledge of the ion and neutral distribution functions as a function of angle and velocity, in addition to modeling the gas-surface reactions. In order to address these needs, we have developed and integrated a suite of models to simulate the etching process from the plasma reactor level to the feature profile evolution level. This arrangement allows for a better understanding, control, and prediction of the influence of equipment level process parameters on feature profile evolution. We are currently using the HPEM (Hybrid Plasma Equipment Model) and PCMCM (Plasma Chemistry Monte Carlo Model) to

generate plasma properties and ion and neutral distribution functions for argon/fluorocarbon discharges in a GEC Reference Cell. These quantities are then input to the feature scale model, Simulation of Profile Evolution by Level Sets (SPELS). A surface chemistry model is used to determine the interaction of the incoming species with the substrate material and simulate the evolution of the trench profile. The impact of change of gas pressure and inductive power on the relative flux of CF@sub x@ and F to the wafer, the etch and polymerization rates, and feature profiles will be examined. Comparisons to experimental profiles will also be presented.

10:40am **PS-WeM8 Application of an Integrated Feature Scale Model to Ionized PVD of Cu Barrier and Seed Processes**, ***V. Arunachalam***, *D.G. Coronell, S. Rauf, P.L.G. Ventzek, X.-Y. Liu,* Motorola Inc.

Ionized PVD has emerged as an important process for the deposition of Cu barrier and seed films in high aspect ratio features. Experiments have shown that ionized PVD results in improved bottom and sidewall coverage owing to the highly anisotropic ion fluxes and the resputtering caused by the energetic ions respectively. Our, previous work@footnote 1@ described the analysis of a single deposition step as a seamless integration of equipment, sheath, feature and atomistic level phenomena. We have extended and improved upon our previous model to consider more detailed process issues at the feature scale level. In particular, we have developed a three-dimensional Monte Carlo-based surface moving algorithm capable of simulating the deposition of multi-component films and multiple deposition steps. In this presentation, we demonstrate the applicability of the model to address process integration and the compositional control of multi-component films. The importance of the initial feature geometry, the ability of the depositing material to wet the underlying substrate, and the preferential sputtering of one film constituent over another will be discussed. @FootnoteText@ @footnote 1@ D. Coronell et al. AVS 1998 paper

11:00am **PS-WeM9 Analysis and Simulation of Mask Erosion During Dry Etching**, ***J. Westlinder***, *F. Engelmark, L.B. Jonsson, C. Hedlund, I.V. Katardjiev, H.-O. Blom,* Uppsala University, Sweden

In order to do topography simulations, which is an important part of process simulation, the erosion/growth rates of materials exposed to different complex processes must be determined. The erosion of the mask during plasma etching is becoming increasingly important as the feature size continues to shrink. By using anisotropic wet etching of silicon wafers it is possible to create structures defined by specific crystallographic planes. This results in silicon groove structures consisting of 7-10 µm wide planar surfaces which form various angles with respect to the wafer normal. The structures can then be coated with different materials and processed under standard operating conditions. Since only Si wafers are used the method is fully IC production compatible and can be used directly in production systems. The method is used to analyze the erosion of different mask materials. Data for the angular dependence of the etch rate for different dry etching processes like e.g. RIE and ICP and for different mask materials used in IC manufacturing have been obtained and will be presented. The results are used as input data to the topography simulation software DINESE.

11:20am **PS-WeM10 Characterization of Photoresist Trimming in a Lam TCP9400 With the Aid of a Profile Simulation**, ***V. Vahedi,*** Lam Research Corporation*; S Lin,* Lam Research Corporation, Taiwan*; H.W. Chang,* Lam Research Corporation*; H.J. Tao, C.C. Chen, C.S. Tsai, M.S. Liang,* Taiwan Semiconductor Manufacturing Company

As a result of the lithography limitations in printing photoresist lines below 0.18m, there is a growing interest in reducing the mask linewidth (in a controlled manner) using dry process tools. This process is called photoresist trimming. A typical polysilicon gate film stack for the next generation devices may include photoresist/hardmask/polysilicon/gate oxide. The advantage of photoresist trimming is that it can be done in situ and can be integrated into the process steps. In this paper, we will discuss the challenges and issues with this process. To accelerate the process development & optimization, we are using a profile simulator to understand the basic mechanisms. Typical trim processes include oxygen with other additives. Our proposed mechanisms for photoresist trimming include chemical etching, ion-enhanced etching & physical sputtering. These mechanisms are included in our profile simulation, and the simulation is calibrated with experimental data. We will show quantitative comparison between simulation and experiments. Once calibrated, the simulation can be used to predict profile changes for any line and spacing. The simulation is being used to study photoresist foot removal and CD variations between isolated and dense lines.

Surface Science Division
Room 607 - Session SS2+AS+PS-WeM

Ion-Surface Interactions I

Moderator: L. Hanley, University of Illinois, Chicago

8:20am **SS2+AS+PS-WeM1 Trapping and Desorption of Energetic Cu Atoms on Cu(111) and (001)Surfaces at Grazing Incidence**, ***D.E. Hanson***, *A.F. Voter, J.D. Kress,* Los Alamos National Laboratory*; X.-Y. Liu,* Motorola, Inc.

Cu is widely used as an interconnect in semiconductor chips. It is deposited by ionized physical vapor deposition on sub-micron features that have sidewalls nearly parallel to the incident ion beam. Molecular dynamics (MD) simulations have shown that, for angles of incidence (with respect to normal) up to 20 degrees, the sticking probability is unity for all energies; the impact atom penetrates and loses all of its kinetic energy to the surface. As the impact angle increases, the probability for the impact atom to reflect increases, reducing the sticking probability. Surprisingly, for angles above 70 degrees, the sticking probability increases with impact angle. We have performed MD simulations of Cu atoms impacting both Cu(111) and (001) surfaces at grazing incidence and find that this unexpected increase in sticking probability is a consequence of trapping (or surface skipping). An energetic Cu atom (10 ¾ E ¾ 100 eV) can become trapped by the mean attractive potential above the surface, oscillating normal to the surface. While in this trapped state, it can traverse hundreds of Å as it dissipates energy to the surface. Until the atom either desorbs or comes to rest, it experiences an average energy loss rate that is piecewise linear, typically comprised of two or more roughly linear (dE/dt = constant) regions. The process can be characterized by two parameters: the desorption probability at each oscillation and an average energy loss rate (per oscillation) that is independent of energy. These parameter values are the same for both the (111) and (001) surfaces. A phenomenological model based on these parameters is presented, and the predictions of sticking probability, average energy transfer to the surface, and total distance traveled along the surface, agree with full MD simulations. The dependence of the desorption probability on the surface temperature, was also studied.

8:40am **SS2+AS+PS-WeM2 Dynamics of NO@super +@ Abstraction of Oxygen on Al(111)**, ***M. Maazouz***, *P.L. Maazouz, D.C. Jacobs,* University of Notre Dame

Energetic collisions between molecules and surfaces can activate a number of reaction processes, such as electron transfer, activated dissociative chemisorption, dissociative scattering, atom abstraction, and sputtering. The branching into each of these channels can be affected by the initial internal energy (electronic, vibrational, and rotational) and collision energy of the molecule. Reactive collisions of NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v=1) with oxygen-covered Al(111) are explored across a range of hyperthermal energies (5-80 eV). A laser forms the incident ions from the neutral NO via resonance-enhanced multiphoton ionization (REMPI). This produces NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v) in a selected vibrational level (v=0-6) of the ground electronic state. Scattered products include O@super -@, NO@super -@, and NO@sub 2@@super -@. The latter product arises from an atom abstraction channel and is the main focus for the present study. The NO@sub 2@@super -@ formation shows a strong dependence on the oxygen coverage and the NO@super +@ primary energy. Detailed reaction mechanisms leading to NO@sub 2@@super-@ emergence will be discussed.

9:00am **SS2+AS+PS-WeM3 Oxygen Negative Ion Emission from Al(100) Bombarded by Li@super+@ Ions**, ***J.A. Yarmoff***, *W.K. Wang, B.-L. Young, B.C. Corbitt,* University of California, Riverside*; Z. Sroubek,* Academy of Sciences of Czech Republic

The intensity of oxygen negative ions sputtered from metal surfaces (V, Mo, Cu) by rare gas ions is known to increase by up to 3 orders of magnitude when the surface work function is lowered by alkali metal adsorption. A resonant charge transfer process from the surface bands to the oxygen affinity level is apparently responsible for the negative ion formation, and such a process is strongly dependent on the surface potential. We have measured the intensities and kinetic energy distributions of O@super-@ sputtered from Al(100) via bombardment by 200 eV Li@super+@ ions. In contrast to experiments with rare gas ions, the O@super-@ intensity is found to be relatively independent of the work function changes induced by Cs deposition (@DELTA@@phi@ = - 3 eV). For O@super-@ kinetic energies above 20 eV there is no increase in the yield,

and it increases by only a factor of 2-3 at lower O@super-@ kinetic energies. The energy distribution depends exponentially upon the O@super-@ kinetic energy, and has a cutoff at about 120 eV. These results suggest that the yield of oxygen particles sputtered from clean Al(100) by Li@super+@ is already nearly completely ionized due to the local potential perturbation caused by the projectile. Thus, a further lowering of the surface potential by the deposition of alkali adsorbates has little effect. This is clear evidence of the localized nature of the resonant charge exchange process, and the first evidence that such a local effect can be induced by the primary particle.

9:20am **SS2+AS+PS-WeM4 Matrix Dependent He+ Neutralization by Adsorbates: An ISS Study of S and Cl on TiO@sub 2@(110)**, ***W. Hebenstreit,*** *E.L.D. Hebenstreit, U. Diebold,* Tulane University

We have studied the adsorption of S and Cl on TiO@sub 2@(110) with low-energy He@super +@ ion scattering spectroscopy (ISS) , X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Because of its high surface sensitivity, ISS is ideally suited to determine the chemical composition of surfaces. While it is well known that quantification of ISS spectra is influenced by trajectory-dependent blocking, the element-specific neutralization of the probing ion is generally assumed not to be matrix dependent. We found that the neutralization of He+ ions (400 - 2450 eV, scattering angle 139°) scattered on Cl or S (adsorbed on TiO@sub 2@(110)), depends strongly on sample pretreatment and adsorption site. Cl (~ 1 ML) and S (~ 2/3 ML) give rise to pronounced peaks in ISS spectra when adsorbed on the sputtered TiO2 sample (1 keV Ar@super +@, flux 1.5 10@super 16@ cm@super -2@), but both species cannot be detected after adsorption at RT on the annealed, stoichiometric TiO@sub 2@(110) surface (coverage ~ 1/3 ML). STM shows that the adsorbates are located on the rows of 5-fold coordinated Ti atoms. When dosed at 573 K, S adsorbs at the position of bridging oxygen atoms, where it forms a (1x3) superstructure. In this case S becomes "visible" again for ISS. All spectra (on sputtered and annealed substrates) show a decrease in the O and Ti ISS signal due to blocking induced by the adsorbates. Subsurface positions of the adsorbates in the "invisible cases" can be excluded by STM. The difference in neutralization is due to different electronic structures of the substrate surface: (a) semiconducting with a 3 eV band gap when annealed; (b) metallic due to defect states and oxygen deficiency after sputtering. In case of S located at the position of bridging oxygens, neutralization is affected by the different local bonding.

9:40am **SS2+AS+PS-WeM5 Hyperhhermal Ion - Surface Interactions**, ***J.W. Rabalais,*** University of Houston **INVITED**

The chemical and physical phenomena accessible by means of low energy ion beams on surfaces will be discussed. Such energetic reactive ions can stimulate selected physical and chemical processes, such as film deposition, growth, synthesis, and shallow implantation within a nonequilibrium UHV environment. The 'low energy' or 'hyperthermal' range is considered to be 5 eV to a few keV. The lower limit is of the order of chemical bond energies. In this limit, chemical bonding interactions become significant, the binary-collision approximation (BCA) becomes questionable, and inelastic interactions can alter the ion trajectories. In the high energy limit, the sputtering yield becomes equivalent to or higher than the beam flux, classical ion trajectory simulations using the BCA provide a satisfactory description of the collision events, and the impinging ions are implanted in the subsurface layers. Mass-selected ion beam deposition (IBD) allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The advantages of IBD for stimulation of chemical reactions, control of film stoichiometry, low temperature epitaxy, good film-substrate adhesion, and for growth of materials with metastable structures, isotopic purity, and high densities will be contrasted with the disadvantages, such as production of defects, imperfections, and amorphous materials and the limited thicknesses of IBD films. Examples of the use of mass- and energy-selected beams for hyperthermal surface reactions, film growth, synergism between ion energy and substrate temperature, and shallow implantation will include: Si+ ion homoepitaxy, the growth SiO2 from pulsed Si+ and O+ beams, low energy Ti+ beams for growth of titanium silicide on silicon and mixed Ti-Al oxides on sapphire (a-Al2O3), growth of diamond-like carbon, growth of Ag(111) on a Ni(100) surface, and survival probabilities of scattered TiClx cluster ions.

10:20am **SS2+AS+PS-WeM7 Dissociation and Energy Distribution Processes in XY@super -@(CO@sub 2@)@sub n@ (XY = ICl, I@sub 2@, and Br@sub 2@) Collision onto Silicon Surface**, ***S. Koizumi,*** Genesis Research Institute, Inc., Japan*; H. Yasumatsu, A. Terasaki, T. Kondow,* Toyota Technological Institute, Japan

Collisional dissociation induced by impact of a cluster anion, ICl@sup -@(CO@sub 2@)@sub n@ (n = 0 - 20), onto a silicon surface were studied by measuring the branching fractions of the ICl@sup -@ dissociation and the translational energies of the product anions as functions of n and the collision energy (per ICl@sup -@) of ICl@sup -@(CO@sub 2@)@sub n@ in an apparatus consisting of a tandem time-of-flight mass spectrometer. It was found that the branching fraction of the ICl@sup -@ dissociation did not change with n at the collision energies of 30 - 70 eV. Molecular dynamics simulation showed that the impinging core ion, ICl@sup -@, tends to orient with the molecular axis of the core ion being at the angle of 55 ° with respect to the surface normal, whereas in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ (X = Br, I) collision, the molecular axis of the X@sub 2@@sup -@ core ion being in parallel to the surface plane. This finding together with prominent wedge effect in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ collision leads us to conclude that the CO@sub 2@ molecules do not work as 'wedge' in the ICl@sup -@(CO@sub 2@)@sub n@ collision because of the unfavorable orientation of the incoming cluster anion. No discernible cage effect could also be related to the orientation. The translational energies of the product anions were interpreted in terms of energy redistribution of the collision energy among the degrees of freedom of the cluster anion and the surface atoms involved in the collision. It was also found that the I and Cl product ions reach quasi-equilibrium with the surface from the measurement of these translational energy distributions.

10:40am **SS2+AS+PS-WeM8 Angle Resolved Measurements of Ions and Neutrals Scattered from HOPG Surfaces upon Hyperthermal Glancing Incidence Irradiation with Large Polyatomic Ions: Charge Changing and Impact Orientation Phenomena**, *M. Hillenkamp, J. Pfister,* ***M. Kappes,*** University of Karlsruhe, Germany*; R. Webb,* University of Surrey, United Kingdom

We have scattered a series of polyaromatic hydrocarbons and various fullerenes from graphite at hyperthermal kinetic energies (100-5000eV) under glancing incidence (75 degrees with respect to the surface normal). Resulting cations, anions and fast neutrals have been studied with a secondary time-of-flight mass spectrometer/detector rotatable about the scattering plane. The corresponding angular distributions have been compared to those obtained upon irradiation of HOPG with He@super +@ and Xe@super +@ ion beams under otherwise identical conditions. Molecular projectiles were typically studied as either singly or multiply charged parent cations. In addition to dominant neutralization, we also observe the scattering of smaller amounts of both cations and anions (parents and fragments). We discuss the relative yields of charge states in terms of charge transfer rate theories as well as in terms of postcollision decay processes (e.g. delayed electron loss). In comparing the surprisingly narrow (and near Gaussian) angular distributions determined for fast neutrals from fullerene scattering with those recorded for xenon, we find that while Xe is specularly scattered over the full energy range studied, fullerenes are scattered subspecularly - with the deviation from specular angle increasing with increasing collision energy. Molecular dynamics simulations with Brenner potentials suggest that this effect results from a combination of the comparatively long (>300 fesec) "turnaround " time of the molecular projectile and a significant perpendicular deformation of the layered target on the collision time scale. For the topologically much more anisotropic polyaromatic hydrocarbon projectiles we find structured fast neutral angular distributions suggestive of a simple dependence between impact orientation and scattering angle

11:00am **SS2+AS+PS-WeM9 Surface Structure Determination by Angle-Resolved Mass Spectroscopy of Recoiled Ions**, ***G.S. Herman,*** Pacific Northwest National Laboratory

Low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) are powerful techniques for the determination of surface composition and structure. The combination of time-of-flight methods with an electrostatic time focussing analyzer has recently resulted in a new technique - mass-spectroscopy of recoiled ions (MSRI).@footnote 1@ The MSRI technique has an advantage over LEIS and DRS in that it has much higher mass-resolution and sensitivities. Results related to the exchange of @super 18@O into samples will be presented to illustrate the high mass-resolution. Furthermore, recent results indicate that in the angle-resolved mode, structural determinations can be performed. Angle-resolved MSRI (AR-

MSRI) results will be presented for CeO@sub 2@(001) and TiO@sub 2@(001)-Anatase films grown on SrTiO@sub 3@(001) substrates by molecular beam epitaxy and chemical vapor deposition, respectively. The experimental data are fit to calculations using the scattering and recoiling imaging code based on the binary collision approximation.@footnote 2@ The ideal CeO@sub 2@(001) surface is polar and predicted to be unstable. However, LEED results indicate that a sharp (1x1) pattern can be obtained. The structural model determined by AR-MSRI consists of an oxygen-terminated surface with a half monolayer of oxygen removed. This structure is consistent with a model based on the reduction of the surface dipole moment. The TiO@sub 2@(001)-Anatase surface has only recently been experimentally investigated in much detail. LEED measurements indicate that the surface undergoes a (1x4) reconstruction after a sputter and anneal cycle. A comparison between experiment and theory for several models for this reconstruction will be presented. @FootnoteText@ @footnote 1@ K. Eipers-Smith, K. Waters, and J.A. Schultz, J. Am. Ceram. Soc. 76, 284 (1993). @footnote 2@ V. Bykov, C. Kim, M.M. Sung, K.J. Boyd, S.S. Todorov, and J.W. Rabalais, Nucl. Instr. And Meth. In Phys. Res. B 114, 371 (1996).

11:20am **SS2+AS+PS-WeM10 Depth Information in Direct Recoiling Peak Shapes: Simulations from Model Surfaces**, ***M. Tassotto,*** Oregon State University*; P.R. Watson,* Oregon State University, U.S.

Direct recoil spectrometry (DRS) has been used in the past to study adsorbate surface structures, chemisorption processes, and average orientations of molecules at surfaces. In these studies, DRS has experimentally been proven to be very surface sensitive. Information on surface structure and composition is primarily based on the analysis of DR peak intensities from the time-of-flight (TOF) spectra. These DR peaks frequently exhibit long tails to higher TOF which often overlap with neighboring peaks. It is common practice to obtain intensities from TOF spectra by integrating the DR peak areas over narrow time windows. Unfortunately, quantitative analysis is complicated by a lack of accurate background removal and only the use of relative intensity variations is possible. In this study, the MARLOWE computer code has been applied to calculate the trajectories of atoms recoiling from both simple and more complex model surfaces (diamond and alkane polymers, respectively) while the depth from which recoiled particles originated was recorded. The DR peak itself as well as the long TOF tail to lower energies contain depth-related information. Near the peak maximum recoils originate from mainly the first atomic layer, supporting the high surface sensitivity of DRS. The initial portions of the tail of the peak provide an approximate atomic depth profile but at longer TOF the tail contains recoils that were produced by several mechanisms from a wide variety of depths. The trajectory calculations have been converted to actual TOF spectra which allows comparison with experimental data from the literature. Here it is important to account for varying detector efficiencies as well as broadening of the simulated DR peak due to the finite pulse width of the ion beam. The MARLOWE calculations make DR peak deconvolution possible. This leads to accurate background removal in determining atomic ratios.

11:40am **SS2+AS+PS-WeM11 Hyperthermal-energy Ion Scattering on Si(100)**, ***C.L. Quinteros,*** *S.I. Tzanev, D.C. Jacobs,* University of Notre Dame

Ion-surface scattering experiments on a Si(100) surface are presented, introducing a new gas/surface experimental system with unique capabilities. Using a Colutron type source, an ion beam with energies between 5-300 eV can be generated. The ions are extracted, accelerated, mass-selected by a Wein filter, decelerated and focused on the surface target. Scattered ions and neutral products are mass- and energy-resolved with a fully rotatable, differentially-pumped detector that includes an ionization source for detection of neutrals, a cylindrical electrostatic analyzer for energy selection, and a quadrupole mass spectrometer for mass selection of the energy-filtered particles. Incident angles between 0-90° and scattering angles between 0-150° can be accessed by independent rotation of the sample manipulator and the detector. A complement of surface analysis techniques (LEED, Scanning Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, and a Kelvin Probe) monitor surface modifications resulting from ion-beam exposure. The surface sample can be cooled to 80K through a liquid nitrogen reservoir or resistively heated to 1000K. The hyperthermal energy range spans from thermal energies (<1eV), where chemical interactions produce inelastic scattering events, to the low energy regime (1-5 keV), where predominantly elastic scattering occurs. We present scattering results for a series of different projectiles on Si(100) that bridge these two energy regimes. The charge state and energy distributions of the scattered products are reported as a function of collision energy and scattering angle.

Plasma Science and Technology Division
Room 612 - Session PS+SS-WeA

Ion-Surface Interactions II

Moderator: C.I.H. Ashby, Sandia National Laboratories

2:00pm **PS+SS-WeA1 How Does Ion Bombardment Produce Enhanced Etching?**, ***P.G.M. Sebel***[1], *L.J.F. Hermans, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

Etching of Si by XeF@sub 2@ is enhanced considerably by ion bombardment. The role of the reaction layer in this process is studied in a multiple-beam setup at room temperature. One of the main reaction products, SiF@sub 4@, is formed in this layer. During spontaneous etching a thick reaction layer with a chain-like Si@sub x@F@sub y@ structure is formed.@footnote 1@ From ion pulse experiments on a slow time scale (100 s), it is concluded that this reaction layer is depleted of fluorine by the ion bombardment. This thinner reaction layer leads to a lower spontaneous SiF@sub 4@ formation. The depletion of the reaction layer is supported by model calculations. Despite this lower spontaneous contribution, the release of reaction products on a depleted reaction layer under ion bombardment is enhanced by chemical and physical sputtering. However, to produce more reaction products, more reactants (XeF@sub 2@) have to adsorb. This raises the question: "How does ion bombardment cause XeF@sub 2@ to have an increased sticking probability".@footnote2@ From ion pulse measurements on a fast time scale (1 s) it is concluded that on a depleted reaction layer XeF@sub 2@ mainly sticks on dangling bonds with a sticking probability of 0.71. By contrast, on a thick reaction layer the adsorption probability of XeF@sub 2@ is determined by the much lower sticking probability of 0.08 on SiF@sub 2@ surface species. This explains the enhanced sticking probability under ion bombardment and shows that a depleted reaction layer is a prerequisite for enhanced etching under ion bombardment. @FootnoteText@ @footnote 1@ M.J.M. Vugts, M.F.A. Eurlings, L.J.F. Hermans, and H.C.W. Beijerinck, J. Vac. Sci. Technol. A 14, 2780 (1996) @footnote 2@Y. Tu, T.J. Chang, and H.F. Winters, Phys. Rev. B. 23, 823 (1981)

2:20pm **PS+SS-WeA2 Desorption Species from Fluorocarbon Film by Ar@super +@ Ion Beam Bombardment**, ***M. Hayashi***, *K. Karahashi,* Fujitsu Laboratories Ltd., Japan

Fluorocarbon films are formed on wafers and chamber walls in etching processes with fluorocarbon plasmas.@footnote 1,2@ Desorption species from them during etching have a lot of influences on Si device fabrication, for example, formation of side wall protection films in etched holes and fluctuation of plasma components in the near-surface region of a wafer. We succeeded in detecting the species that are desorbed from fluorocarbon films by ion bombardment. In this study, we constructed a new apparatus in order to investigate desorption species from fluorocarbon films. The measured fluorocarbon films were deposited on a Si wafer by exposing it to a C@sub 2@F@sub 6@ plasma in an inductively coupled plasma (ICP) reactor. The species desorbed by Ar@super +@ ion beam bombardment at a few keV into the films were detected using a quadrupole mass spectrometer (QMS). The film characteristics were evaluated simultaneously by x-ray photoelectron spectroscopy (XPS), and we discuss the correlation between the desorption species and the film characteristics. QMS spectra that were measured during the Ar@super +@ ion beam bombardment of the fluorocarbon films show many sorts of dissociated C@sub x@F@sub y@. CF@sub 3@@super +@ is a dominant QMS peak in the fragment pattern, and this indicates that CF@sub 4@ is a dominant desorption species. Besides, some large desorption species are recognized because of the detected large fragment ions of C@sub 3@F@sub 3@@super +@, C@sub 3@F@sub 5@@super +@, and so on. The ratios among CF, CF@sub 2@, CF@sub 3@, and CF@sub 4@ species, which were measured with the appearance energies, indicate that CF@sub 4@ is a dominant desorption species with the ratio of 80 % among them at the beginning of bombardment. However, continuous ion bombardment causes the CF ratio to increase instead of decrease in the CF@sub 4@ ratio. This demonstrates the change in film characteristics from F-rich to C-rich, which was evaluated by XPS measurement. Moreover, The formation of C-rich film also corresponds to a reduction in total amount of desorption species. @FootnoteText@ @footnote 1@K. Takahashi, M. Hori, and T. Goto, J. Vac. Sci. Technol. A 14, 2011 (1996). @footnote 2@T. Shirafuji, W. Stoffels, H. Moriguchi, and K. Tachibana, J. Vac. Sci. Technol. A 15, 209 (1997).

2:40pm **PS+SS-WeA3 NH@sub 3@ / Cl@sub 2@ Gas Assisted Etching of Copper with Focused Ion Beams**, ***K. Edinger***, University of Maryland

With the implementation of copper instead of aluminum as metallization layer in high performance integrated circuits, the use of gas assisted etching for focused ion beam (FIB) based failure analysis and circuit rewiring becomes increasingly important. In the present study the effects of exposing a copper substrate to a mixture of chlorine (Cl@sub 2@) and anhydrous ammonia (NH@sub 3@) during ion bombardment have been investigated. The exposure of the copper surface to chlorine or to NH@sub 3@-Cl@sub 2@ mixtures leads to the formation of a reaction layer. The thickness of this layer and its texture depends on the FIB parameters such as ion beam dwell time, gas pressure and the NH@sub 3@ to Cl@sub 2@ flux ratio. In addition, the experiments indicate that the formation of the reaction layer is enhanced in areas that have been previously exposed (i.e. damaged) with an ion beam. The etch yield shows a strong dependence on the ion beam dwell time and the gas flux. For short dwell times and low NH@sub 3@ and Cl@sub 2@ flux an up to 10-fold increase over physical sputtering could be achieved. With increasing Cl@sub 2@ flux the etch rate decreased and the maximum in the etch yield shifted to longer dwell times, indicating changes in the adsorption kinetics of the two gases.

3:00pm **PS+SS-WeA4 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Mo**, ***S.L. Anderson***, *A. Lapicki, K.J. Boyd, M. Aizawa,* University of Utah

Results of low-energy ion beam deposition of Cu@super +@ and Cu@sub 2@@super +@ on polycrystalline molybdenum at energies from 5 to 220 eV are presented. Thermodynamics in this system favor Cu diffusion to the surface. At low energies, Cu@super +@ is deposited on the surface with a sticking probability of ~0.6. As the energy is increased above 100 eV, stable subplantation of the Cu is observed. This threshold is substantially higher than expected for penetration; it seems likely that penetration occurs at lower energies, however, migration of the subplanted Cu to the surface is efficient. The results for Cu@sub 2@@super +@ are different in that subsurface copper is observed at energies down to 40 eV (20 eV/atom). This counterintuitive result is tentatively explained by the formation of complex defects which stabilize subplanted Cu. Possible defect production mechanisms are explored using variable-angle XPS, XAES and molecular dynamics simulations.

3:20pm **PS+SS-WeA5 Ion Solid Surface Interactions in IMP Cu PVD**, ***X.-Y. Liu***, *M.S. Daw, D.G. Coronell, V. Arunachalam, C.-L. Liu,* Motorola Semiconductor Products Sector*; J.D. Kress, D.E. Hanson, A.F. Voter,* Los Alamos National Laboratory

A thorough understanding of ion-solid surface interactions is important for predictive modeling of ionized mass plasma (IMP) Cu physical vapor deposition (PVD) at feature scales. Besides sticking coefficients and sputter yields, fundamental parameters such as angular distributions of sputtered and reflected particles, and thermal accommodation coefficient are also needed as inputs for the feature scale process simulator. Molecular dynamics (MD) simulations can be used to provide pertinent information and physical insights. In this presentation, we'll demonstrate our recent MD results for Ar+/Cu and Cu+/Cu systems, as a function of hyperthermal ion energies and impact angles. The issue of integrating different sticking coefficients for different surface "roughness" will be addressed, based on ion travel distance analysis. We have found that the sputtered particle distributions are not cosine, but can be described by a simple Gaussian-like formula. Reflection characteristics were also analyzed and compared with simple analytical assumptions. Finally, the existing trends in the MD results from the systems will be discussed in terms of interaction strength, ion energy and impact angle.

3:40pm **PS+SS-WeA6 Deposition and Etching Using Fluorocarbon Ions: Molecular Dynamics Simulations**, ***C.F. Abrams***[2], *D.B. Graves,* University of California, Berkeley

SiO@sub 2@ etch processes use fluorocarbon (FC) plasmas to achieve selectivity to Si, SiN, and photoresist. FC plasmas deposit films which slow the etching of these surfaces compared to SiO@sub 2@. Further etch process optimization hinges on understanding these films. Specifically, the mechanisms of Si etching through the FC overlayer remain matters of speculation. We used molecular dynamics simulations of FC ions impacting Si surfaces to understand this process. We developed a Si-C-F interatomic

[1] **PSTD Coburn-Winters Student Award Finalist**

[2] **PSTD Coburn-Winters Student Award Finalist**

potential as an extension of our C-F potential.@footnote 1@ We simulated ion impacts at normal incidence onto a:Si surfaces up to fluences of 4x10@super 16@ cm@super -2@. We examined the effects of ion composition (CF@sub x@ for x=1,2,3) and incident energy (50 @<=@ E@sub i@ @<=@ 200 eV). At low fluences, all ions deposit FC overlayers with significant Si incorporation. We found that CF ions result in net CF@sub x@ deposition, while CF@sub 3@ ions result in net Si etching with a steady-state overlayer thickness that increased with E@sub i@. For example, for 100 eV CF@sub 3@, we observed deposition of 2 equivalent monolayers of C up to a fluence of 4x10@super 15@ cm@super -2@, followed by Si etching (0.065 Si/ion) through a FC film with a steady thickness of 9.5 Å and F:C of 1.6. For CF@sub 2@, the resulting steady-state, deposition or Si etching, depended on E@sub i@, with deposition being favored at the lower energies. A striking result of the simulations is the dynamic character of the FC film during Si etching. Although the composition and thickness of the layer are unchanging at steady-state, F and C atoms are constantly depositing and then being etched by subsequent ion impacts. This `recirculation' of F and C through the overlayer appears to play a key role in Si etching. Mechanisms of both initial film deposition and steady-state etching by FC recirculation will be discussed. @FootnoteText@ @footnote 1@ J Tanaka, C F Abrams, D B Graves. Subm, 46th AVS Intl Sym, 1999.

4:00pm **PS+SS-WeA7 Comparison of Thin-Film Nucleation and Growth from Ion-Beam and Cluster-Beam Deposition: Atomistic Simulations***, **T.A. Plaisted**, S.B. Sinnott,* University of Kentucky

Experimental efforts have examined the formation of diamond-like and tailored polymer films through beam deposition. The results show that strongly adhering hydrocarbon thin films can be generated through the impact of organic ions or small clusters with mica, diamond, or glass surfaces. To study the processes involved in the nucleation and growth of these films we have performed atomistic simulations of beam impacts. Specifically, classical molecular dynamics simulations have been used where the forces are calculated using a many-body, reactive, bond-order potential. Our goal is to better understand the dependence of the film structure the reaction conditions. The simulations show the atomic-scale mechanisms by which the films nucleate and reveal the conditions needed to tailor the structure of the film. They also provide a basis for comparing the nucleation mechanisms and film structures obtained from ion-beam and cluster-beam deposition. @FootnoteText@ This work is supported by the Petroleum Research Fund and the National Science Foundation (CHE-9708049). .

4:20pm **PS+SS-WeA8 Understanding Plasma Polymerization by Mass Selected Ions: 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ Ion Modification of Polystyrene***, **M.B.J. Wijesundara**, L. Hanley,* University of Illinois, Chicago*; B. Ni, S.B. Sinnott,* University of Kentucky

Mass selected polyatomic ions beams can both create new materials similar to plasma polymers and elucidate polyatomic-surface collision mechanisms that are fundamental to plasma polymerization and etching. The fluorocarbon ions are studied here due to their technological relevance, the large number of previous studies on related systems, and their ability to illuminate several fundamental points in polyatomic ion-surface modification and plasma polymerization. Polystyrene has been chosen because it is a typical polymer surface whose lack of heteroatoms facilitates its surface chemical analysis. Previous experiments with 10 - 100 eV SF@sub 5@@super +@ and C@sub 3@F@sub 5@@super +@ indicated different chemistry with polystyrene surfaces.@footnote 1@ This work is continued here by examination of 25 - 50 eV CF@sub 3@@super +@ vs. C@sub 3@F@sub 5@@super +@ ion reactions with polystyrene surfaces using monochromatic x-ray photoelectron spectroscopy and molecular dynamics simulations. These two fluorocarbon ions display significantly different surface chemistry at these low kinetic energies that cannot be explained simply by eV/atom arguments. @FootnoteText@ @footnote 1@E. T. Ada, O. Kornienko, L. Hanley, J. Phys. Chem. B 102, 3959-3966 (1998).

4:40pm **PS+SS-WeA9 Surface Interactions of Plasma-Generated NH@sub 2@ Radicals***, E.R. Fisher, **J.R.D. Peers**, M.L. Steen,* Colorado State University

Ammonia plasmas are used in the microelectronics industry to deposit amorphous hydrogenated silicon nitride (a-SiN@sub x@:H) films. Thin films of a-SiN@sub x@:H are used as gate dielectrics and barrier coatings in microelectronic devices, capacitors in dynamic random access memory (DRAM) cells, and microfabrication of sensors and actuators. Using the imaging of radicals interacting with surfaces (IRIS) technique, we have performed a comprehensive study of the interactions of NH@sub 2@ with a variety of surfaces during NH@sub 3@ plasma processing. The substrates examined were Si(100), Pt, polyimide, polyethylene, and Teflon. In most cases, NH@sub 2@ scattering from the surface was greater than unity, indicating a production of NH@sub 2@ through surface reaction. Removal of charged species from the plasma molecular beam results in a decrease in the scattered NH@sub 2@ signal, indicating that the presence of ions in the plasma is responsible in large part for radical production at the surface. We have examined the dependence of the scattering signal intensity on applied rf plasma power and substrate temperature for all species. In addition, velocity distributions for NH@sub 2@ radicals scattering off the surfaces were measured. Using Monte Carlo simulation methods and assuming a Maxwell-Boltzmann distribution, we determine the translational temperatures of the scattered species. Species scattering off 300 K Si and Pt substrates have a translational temperature of 400±30 K, significantly higher than the substrate temperature, while the translational temperature of species scattering off the polymeric substrates tends to be closer to the substrate temperature. This suggests that the NH@sub 2@ radicals are coming to equilibrium with the polymeric substrates and not with Si or Pt. The temperature of the radicals in the plasma molecular beam itself is 512±8 K at 25 W applied plasma power, indicating that the radicals are cooling by collisions with the substrate surface.

5:00pm **PS+SS-WeA10 FT-IR and XPS Study of Plasma-treated Acrylic Coating Surfaces***, **M.K. Shi**, G.L. Graff, M.E. Gross, P.A. Mounier, M.G. Hall,* Battelle Pacific Northwest National Laboratory

Polymer/metal multilayer structures have many potential optical, display, and packaging applications. A key issue for the successful processing of such multilayer stacks is obtaining good wetting and adhesion at each interface. Low-temperature plasmas have proven to be one of the most efficient technologies for such purposes. Moreover, the effects of plasma treatments are limited typically to the outermost surface layers and the process is fully compatible with the polymer/metal multilayers cluster tools. We studied the interaction of RF (13.56 MHz)plasmas with an acrylic (tripropyleneglycol-diacrylate)coating surface using FT-IR and XPS. The acrylic coating, with thickness varying from 100 Å to 2 µm, was deposited onto an Al metallized PET substrate by vacuum flash evaporation of the acrylic monomer and subsequent UV-curing. FT-IR measurements showed the destruction of initial ester (O-C=O) and ether (C-O-C) groups, and the ablation of H from C-H bonds after plasma treatments. These effects were accompanied by the formation of carbonyl (R-C=O) and/or acid (R-COOH) groups, and the development of graphite-like C-C structures. The spectral features are similar for N@sub 2@and O@sub 2@ plasma-treated surfaces, no N-containing absorption peaks can be identified for the N@sub 2@ plasma-treated surface. XPS measurements confirmed the loss of the ester (O=C-O) and ether (C-O-C) bonds with respect to the C-C (C-H) peak, and the formation of carbonyl groups. The spectra further showed that approximately 10% of atomic N have been incorporated into the surface after N@sub 2@ plasma treatment. These results showed clearly that FT-IR and XPS are complementary techniques for the characterization of plasma-modified polymer surfaces. The possible plasma/acrylic coating interaction mechanisms will be discussed.

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

Dielectric Etching

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

2:00pm **PS-WeA1 Dielectric Etching : From Oxide to Low k Dielectrics***, **P. Berruyer**,* LETI (CEA-Grenoble), France*; O. Joubert, D. Fuard,* CNRS-LTM Grenoble, France*; C. Verove,* ST-Microelectronics, France*; M. Assous,* LETI (CEA-Grenoble), France*; R. Blanc, H. Feldis,* ST-Microelectronics, France*; E. Tabouret,* LETI (CEA-Grenoble), France*; Y. Morand,* ST-Microelectronics, France **INVITED**

Dielectric etching for interconnection is one of the most critical processes of the ULSI technology. Up to now oxide has been used as inter-metal dielectric with an aluminum based metallisation. The well known issue of contact and vias etch process is the etch-stop phenomenon occurring in high aspect ratio structures, if highly selective process is required. The introduction of copper and thus dual damascene architectures, has increased the number of dielectric etch processes required in the fabrication of ICs. Moreover the level of difficulty of these processes has increased : aspect ratio can be higher than it is in contact and vias, holes but also lines can be etched and high selectivity to nitride is required. If the

introduction of copper has led to a more critical oxide etch process, the introduction of low k material dielectrics will lead to a break off in dielectric etch processes. These low k materials can be either mineral or organic with various porosity. This paper deals with the different etching processes and plasma source required for these different dielectrics. First of all, process performances such as profile, selectivity, CD, trenching, µloading, etch stop, yield, plasma induced damage will be studied as a function of process parameters. We will point out that, if etch stop in high aspect ratio structures is the main issue in oxide etch, profile control is the main issue of the etching of low k polymer materials (SiLK). Mechanisms related with these 2 issues will be proposed. Process conditions required for the etching of aerogel materials will also be discussed. Then, taking into account the process performances and limitations obtained previously, different schemes of dual damascene structures with copper metallisation will be compared. @FootnoteText@ @footnote 1@ This work has been carried out in the frame of GRESSI consortium between CEA.G-LETI and FRANCE TELECOM-CNET

2:40pm **PS-WeA3 Surface Kinetics Study of Silicon Dioxide Etching with Fluorocarbons in Inductively-coupled Plasmas**, ***H. Chae***, *H.H. Sawin,* Massachusetts Institute of Technology

High-density fluorocarbon plasma for silicon dioxide etching has various ion and neutral compounds. Depending upon the plasma condition, many difficulties arise such as RIE lag, inverse RIE lag, etch stop, and low selectivity of photoresist. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as function of ion bombardment energy, ion impinging angle, ion-to-neutral flux ratio, which are necessary for profile evolution modeling of silicon dioxide etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to differentially pumped side chambers. Surface reaction is studied by measuring etching and deposition rate with quartz crystal microbalance (QCM). At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. Etching or deposition rate is measured with QCM as function of ion acceleration energy, ion-impinging angle, ion-to-neutral flux ratio, with various fluorocarbon plasmas. Ion flux is characterized by measuring physical sputtering rate of oxide with Ar plasma and neutral flux is characterized by measuring fluorocarbon deposition rate with CHF@sub 3@ plasma. Three different fluorocarbon plasmas-C@sub 2@HF@sub 5@, C@sub 2@HF@sub 5@ + C@sub 2@H@sub 4@F@sub 2@, C@sub 4@F@sub 8@- are studied for oxide and photoresist etching. Hydrogen rich chemistry - C@sub 2@HF@sub 5@ + C@sub 2@H@sub 4@F@sub 2@ (20%)- has high deposition rate at low ion bombardment energy less than 100V. That hydrogen rich chemistry has the smallest neutral flux and the largest ion flux among them while C@sub 4@F@sub 8@ has the largest neutral flux and the smallest ion flux at the same given power and flowrate.

3:00pm **PS-WeA4 Chemical Bonding Arrangement Approach for Selective Radical Generation in High-density, Low-pressure Fluorocarbon Plasma**, ***S. Samukawa***, *T. Mukai,* NEC Corporation, Japan

Generally, SiO@sub 2@ etching is done with fluorocarbon gases so that a fluoropolymer layer is deposited on the underlying silicon to enhance the etching selectivity for SiO@sub 2@ over silicon and silicon nitride. CF@sub 2@ radicals have been used as the main gas precursor for polymer deposition, and CF@sub 3@@super +@ ions have been the dominant etchant for SiO@sub 2@ films. The CF@sub 3@@super +@ ions are mainly generated from CF@sub 3@ radicals. Thus, to realize high-performance SiO@sub 2@ etching, precise control of CF@sub 2@ and CF@sub 3@ radicals in the fluorocarbon gas plasmas is indispensable. In this paper, we discuss how the efficiency of radical generation is affected by the chemical bonding of gas molecules in the fluorocarbon gas plasma. We found that dissociation of the C=C and C-I bonds are 5 times and 6 times higher than that of the C-C bond in a fluorocarbon gas plasma. As a result, a C@sub 2@F@sub 4@ plasma could generate a higher density of CF@sub 2@ radicals than a C@sub 4@F@sub 8@ plasma. The CF@sub 3@I is also efficient source of CF@sub 3@ radicals (CF@sub 3@@super +@ ions). By changing the gas-flow ratio of the CF@sub 3@I and C@sub 2@F@sub 4@ mixture, the density ratios of CF@sub 2@ and CF@sub 3@ (CF@sub 3@@super +@) could be independently controlled and high performance SiO@sub 2@ etching could be obtained. The appropriate choice of chemical bonding in the fluorocarbon gases is a useful way to control the generation of radicals and ions for SiO@sub 2@ etching.

3:20pm **PS-WeA5 Flux Control for High-Aspect-Ratio Contact Hole Etching**, ***T. Tatsumi***, *M. Matsui, Y. Hikosaka, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between SiO@sub 2@ etch rates and incident fluxes of reactive species in a dual-frequency (27/0.8 MHz) parallel plate system@super 1@ was evaluated by using various in-situ measurements tools, such as infrared laser absorption spectroscopy (IRLAS), quadruple mass spectroscopy (QMS), and optical emission spectroscopy (OES). The thickness and composition of a fluorocarbon (C-F) polymer layer on the etched SiO@sub 2@ surface was also measured by XPS. The SiO@sub 2@ etch rate in a large area depends on both the total amount of F (@GAMMA@@sub F-total@) in the C-F reactive species and the energy at the SiO@sub 2@ surface. @GAMMA@@sub F-total@ could be estimated from the net fluxes calculated by using F, CF, CF@sub 2@, and CF@sub 3@ radical densities.@super 2@ Reaction energy depends on the total amount of ion fluxes (@GAMMA@@sub ion@) which is a function of the plasma density (n@sub e@) at the sheath edge, the acceleration energy of ions (assumed to be peak to peak voltage V@sub pp@), and the energy loss in the C-F polymer layer. The thickness of C-F polymer layer (T@sub C-F@) could be varied by the amount of both the CF@sub x@ species and the oxygen radical in the incident fluxes, the oxygen out-flux from the SiO@sub 2@, @GAMMA@@sub ion@, and V@sub pp@. Excess CF@sub x@ reactive species induced the thicker polymer layer (>1 nm). The thick polymer layer of 5 nm corresponded to the energy loss of about 1 kV. When using @GAMMA@@sub F-total@ (CF@sub x@), @GAMMA@@sub ion@ (n@sub e@), V@sub pp@, and T@sub C-F@, we can conduct in-situ monitoring of the SiO@sub 2@ etch rate. The etch rate at the bottom of contact hole was also evaluated. The decrease in SiO@sub 2@ etch rate in the fine holes can be similarly explained by either the lack of etchant or the lack of reaction energy. In order to obtain the high aspect ratio contact holes, it is important to suppress the excess formation of the C-F polymer layer on the etched surface. Increasing the oxygen flux is one way to do this, however it decreases the selectivity to the resist mask and the SiN. Therefore, higher ion flux is needed to obtain an etching process that enables us to achieve the deeper contact holes with higher selectivity. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., Jpn. J. Appl. Phys., 37 (1998) 2394. @footnote 2@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999); to be published.

3:40pm **PS-WeA6 Etching Chemistry and Kinetics of BCB Low-k Dielectric Films**, ***S.A. Vitale***, *H.H. Sawin,* Massachusetts Institute of Technology

Etching of BCB has been performed in a high density inductively coupled plasma reactor using O2 + hydrofluorocarbons, O2 + F2, and O2 + Cl2 chemistries. The etch rates of the films and the selectivities over oxide are correlated to the flux of ions and reactive radicals to the wafer. Species identification and fluxes to the wafer are determined by mass spectrometry, two gridded ion energy and current analyzers, and a Langmuir probe. Etch rates at many points on the wafer are simultaneously measured using Full Wafer Interferometry. Etching yields as a function of ion bombardment energy, neutral/ion flux ratio, and ion impingement angle are quantitatively determined using a novel plasma beam / QCM system. It is proposed that in high density, low pressure plasmas, the etching rate can be limited by the radical flux and by the ion flux to the wafer under different conditions. The selectivity of BCB etching over oxide etching is greatest for etchant gas compositions of approximately 20-40% halogenated gas in oxygen. Selectivity over oxide greater than 20 has been realized with BCB etch rates over 1 um/min . The implications of these results for the integration of BCB as a low-K dielectric into a copper dual damascene architecture are discussed.

4:00pm **PS-WeA7 The Effect of Capacitive Coupling on Inductively Coupled Fluorocarbon Plasma Processing**, ***M. Schaepkens***, *N.R. Rueger,* State University of New York at Albany*; J.J. Beulens,* ASM International, The Netherlands*; I. Martini, E.A. Sanjuan, X. Li, T.E.F.M. Standaert, P.J. Matsuo, G.S. Oehrlein,* State University of New York at Albany

Different inductively coupled plasma reactors differ in the amount of capacitive coupling, which may influence the plasma process in a non-obvious fashion. We performed a study of inductively coupled fluorocarbon plasmas in which the amount of capacitive coupling was systematically varied. It is found that the plasma density decreases while the electron temperature increases as the amount of capacitive coupling is increased at a constant inductive power level. The rate at which the dielectric (quartz) coupling window is eroded is found to scale with both the peak-to-peak RF voltage and the ion current density, and the dielectric window erosion is found to influence the resulting plasma gas-phase chemistry. The changes in these plasma electrical and chemical characteristics can, on their turn,

have a large impact on the surface processes occurring in inductively coupled fluorocarbon plasmas, such as fluorocarbon deposition, fluorocarbon etching, SiO@sub 2@ etching and Si etching. An important result obtained in this study is that certain plasma etch processes, such as selective SiO@sub 2@-to-Si etching, can benefit to a certain extent from capacitive coupling effects.

4:20pm **PS-WeA8 High Density Plasmas Etching of Low Dielectric Constant Materials**, ***D. Fuard,*** CNRS, France; *O. Joubert,* France Telecom-CNET and CNRS, France; *L. Vallier,* France Telecom-CNET and CNRS

The etching step remains one of the key technological issue for low K integration in advanced CMOS technologies. We have studied the etching mechanisms of SiO@sub2@ masked fluorine free aromatic hydrocarbon polymer. Experiments are performed in a high density plasma helicon source operated at low pressure. Previous work has shown that the SO@sub2@/O@sub2@ chemistry, even if suitable for a good profile control, induces the formation of sulphur-based acids which may generate corrosion latter in the process. In this paper, we present results using sulphur free chemistries based on N@sub2@, H@sub2@ and O@sub2@. First, we have used X-Ray Photoelectron Spectroscopy (XPS) analyses to understand the etch mechanisms of the polymer. XPS analyses reveal that under high energy ion bombardment conditions, the polymer structure is strongly graphitized : C1s binding energy originating from the polymer shifts from 285 to 283.5 eV. The graphitization phenomenon is also dependent on the chemistry used. Without changing the plasma operating conditions, very reactive chemistries, such as pure O@sub2@, prevent the polymer graphitization whereas adding N@sub2@ to O@sub2@ may lead to a severe graphitization by decreasing the chemical component and favoring the physical component of the etch. Using appropriate gas mixture and plasma operating conditions, high aspect ratio contact holes are etched with a good profile control. XPS analyses of the etched structures reveal that the passivation layer formed on the polymer sidewalls is also strongly graphitized, suggesting that the passivation layer originates from the etch products. Some results obtained in other high density plasma tools using identical chemistries will be presented and general conclusion on polymer etching in high density plasmas will be drawn. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

4:40pm **PS-WeA9 A Mechanism of Oxide to Nitride Selective RIE**, ***T. Sakai,*** *T. Ohiwa,* Toshiba Corporation Semiconductor Company, Japan

In highly integrated ULSIs, selective etching of oxide to nitride has been widely used for Self-Aligned Contact (SAC) etching to increase the packing factor. It is known that the CF@sub x@ polymer formed selectively on the nitride surface suppresses Si@sub 3@N@sub 4@ etching. However the origin of selective CF@sub x@ polymer formation is not understood well. We studied the mechanism of oxide to nitride selective etching with focus on selective polymer formation. In CHF@sub 3@-based chemistry, the oxide etch rate decreased slightly from 540 nm/min to 470 nm/min when the cathode temperature was increased from RT to 120 °C. On the contrary, the nitride etch rate decreased abruptly from 720 nm/min at RT to 220 nm/min at 60 °C. XPS analysis showed CF@sub x@ polymer formation on nitride at 60 °C, but no CF@sub x@ polymer at RT. Increase of temperature increases the C/F ratio of the adsorbed species on the surface, therefore CF@sub x@ polymer formation is considered to be enhanced on nitride. Following this result, the temperature in actual SAC etching using C@sub 4@F@sub 8@/CO/Ar chemistry was increased from 20 °C to 70 °C, and the selectivity at the corner of nitride increased from 10 to 18. Further surface analysis of the nitride surface etched in C@sub 4@F@sub 8@/CO/Ar chemistry at 70 °C revealed that the etched nitride surface has C-N bonds. At low temperature, the nitride etching reaction forms volatile etching products of SiF@sub 4@, CFN, C@sub 2@N@sub 2@ and etc., leading to no CF@sub x@ polymer formation similar to oxide. However, at the higher temperature, the higher C concentration of adsorbed species on the nitride surface suppresses the formation of volatile CFN, resulting in remaining of CN compounds, and forms CF@sub x@ polymer. CO, which is the etching product in oxide etching, has a much higher vapor pressure compared to CN compounds. So a difference of CF@sub x@ polymer formation arises between the oxide surface and the nitride surface, resulting in selective etching of oxide to nitride.

5:00pm **PS-WeA10 SiON SAC Etching Technique Using C@sub 4@F@sub 8@/CH@sub 2@F@sub 2@/Ar Plasma for 0.18µm Technology and Beyond**, ***J.H. Kim,*** *J.S. Yu, J.S. Na, J.W. Kim, Y.S. Seol, J.C. Ku, C.K. Ryu, S.J. Oh, S.B. Kim, S.D. Kim, I.H. Choi,* Hyundai Electronics Industries Co. Ltd., Korea

A SAC technique using an oxynitride (SiON) layer as a contact oxide etch barrier has been developed for 0.18µm technology and beyond. Generally, a SAC which uses a SiN etch barrier for 0.25µm technology may exhibit some disadvantages such as wafer warpage, film lifting, transistor reliability degradation, large contact junction leakage, needs for additional anti-reflection coating (ARC) layer, and large parasitic capacitance due to its high dielectric constant. These demerits can be eliminated or improved when the SiON SAC technique is applied. But it is not easy to obtain an oxide etching process with a high selectivity to the SiON etch barrier because of oxygen component within the SiON layer. To overcome this problem, we intentionally introduced excessive Si during the SiON film deposition in order to increase the selectivity to SiON. The developed SiON layer plays the roles of ARC for wordline and bitline photo resist patterning, and side-wall spacer to build a MOS transistor as well as SAC oxide etch barrier. The contact oxide etch was done using C@sub 4@F@sub 8@/CH@sub 2@F@sub 2@/Ar in a dipole ring magnet (DRM) plasma. As the C@sub 4@F@sub 8@ flow rate increases, the oxide etch selectivity to the SiON increases but etch-stop tends to happen. In highly selective SAC oxide etching, it is very important to avoid etch-stop for a wide process window. It was reported that CH@sub 2@F@sub 2@ chemistry helps to widen the process window through its hydrogen effects.@footnote 1@ Our optimized contact oxide etch process showed the high selectivity to SiON larger than 25 and a wide process window (@>=@ 4 sccm) for the C@sub 4@F@sub 8@ flow rate. When the SiON SAC process was applied to a giga-bit DRAM of cell array, there was no short failure between conductive layers. @FootnoteText@ @footnote 1@J.H. Kim et al., The 193rd Meeting of Elecrochem.Soc., Abst. 183, 1998

Manufacturing Science and Technology Group
Room 611 - Session MS+PS-ThM

Environmentally Benign Manufacturing

Moderator: F. Shadman, University of Arizona

8:20am **MS+PS-ThM1 ESH as One of the Key Criteria for Semiconductor Process Development**, ***A. Bowling***, *T. Wooldridge, J. DeGenova, T. Yeakley, T. Gilliland, A. Cheng, L. Moyer,* Texas Instruments Inc. **INVITED**

During the development of advanced semiconductor devices, great benefit has been observed by treating ESH as a key process development specification. Earlier it had been feared that one must sacrifice process performance and/or cost to pursue ESH goals. However, in actuality, the process development engineer has frequently found that a process optimized for ESH also has better performance and lower cost per wafer. This paper will give a number of examples where ESH optimization has produced such performance and cost benefits. These examples include DI-water recycling, dilute SC1 wafer cleaning, wafer rinse optimization, dilute HMDS for resist develop, plasma-enhanced chemical vapor deposition (CVD) chamber cleaning optimization of PFC emissions, capture and recycling of copper plating solutions, copper CVD precursor recovery and recycling, post-metal etch solvent clean optimization, vacuum pump oil reclamation/optimization, and IPA recovery and recycling. The paper will conclude that ESH should be treated as another process performance and cost variable just like etch/deposition rate, non-uniformity, and particle counts.

9:00am **MS+PS-ThM3 The Environmental Impact of Perfluorinated Compounds used in the Semiconductor Industry**, ***R.F. Jewett***, Litmas Corp. **INVITED**

Perfluorinated compounds such as CF@sub 4@, C@sub 2@F@sub 6@, CHF@sub 3@, and others serve as low-toxicity carriers of fluorine for various semiconductor manufacturing processes. The low-toxicity of these chemically stable compounds make the workplace safer, but are a cause of concern when considering their long-term environmental impact. Most PFC's are strong absorbers of infrared radiation. This heat retention, combined with an extremely long atmospheric lifetime makes the environmental impact of continued emission significant and deserving of attention. This paper summarizes the current state of research on the roles of PFC's in the environment, and briefly considers various treatment methods that reduce emissions. There are several commercial systems available which have demonstrated dramatic performance in reducing PFC emissions.

9:40am **MS+PS-ThM5 Optimization of Processing Plasmas in the Semiconductor Industry for Minimal Environmental Impact**, ***J.G. Langan***, Air Products and Chemicals, Inc. **INVITED**

Most processing plasmas used by the semiconductor industry today have been extensively optimized for manufacturing performance. However, this optimization has traditionally not considered environmental impact as part of the performance criteria. Recent measurements have revealed that essentially all processing plasmas emit some form of gaseous by-products or un-reacted source materials which can be categorized as either volatile organic compounds (VOCs), hazardous air pollutants (HAPs), or perfluorinated compounds (PFCs). Although effective abatement solutions exist for some of these compounds they often transfer the problem from one phase to another requiring subsequent treatment. In an effort to develop truly optimized plasma processes we have investigated the operation of high pressure fluorinated gas (NF@sub 3@, C@sub 2@F@sub 6@) plasmas, predominantly used for CVD chamber cleaning applications, to determine which conditions lead to the highest throughput, lowest environmental impact processes. Using a variety of diagnostics; mass spectrometry, FTIR, electrical impedance analysis, and incident ion energy analysis the effect of operating conditions on etch rate, source gas utilization, by-product formation, and positive ion energy distribution functions have been determined. Using the insight gained from these measurements effective strategies have been identified to maximize the performance of CVD chamber cleans while minimizing their environmental impact. This presentation will give an overview of the environmental challenges associated with gaseous emissions from these tools and our efforts to identify viable solutions for chamber cleans in particular and semiconductor processing plasmas in general.

10:20am **MS+PS-ThM7 PFC Abatement in Inductively Coupled Plasma Reactors using O@sub 2@, H@sub 2@ and H@sub 2@O as Additive Gases@footnote 1@**, ***X. Xu***, *M.J. Kushner,* University of Illinois, Urbana

Perfluorinated compounds (PFCs), gases which have large global warming potentials, are widely used in plasma processing for etching and chamber cleaning. Due to under-utilization of the feedstock gases or by-product generation, it is usually necessary to abate emissions of PFCs from plasma processing reactors. Plasma abatement is being developed as one remediation strategy. Previous studies have shown that plasma abatement of, for example, C@sub 2@F@sub 6@ using O@sub 2@ as an additive may be effective in remediating the C@sub 2@F@sub 6@ but may also generate PFC products such as CF@sub 4@. Alternate additive gases may, however, avoid this problem. In this study, the scaling of plasma abatement is investigated using the 2-dimensional Hybrid Plasma Equipment Model (HPEM). Both the plasma etching chamber and downstream plasma burn-box are simulated in order to have realistic entry conditions for the burn-box. O@sub 2@, H@sub 2@, and H@sub 2@O are examined as additive gases in the burn-box. All PFCs in the effluent can generally be remediated in the burn-box at high power deposition with a sufficiently large flow of additive gases. In general CF@sub 4@ generation occurs during abatement of C@sub 2@F@sub 6@ using O@sub 2@ as an additive. CF@sub 4@ is not, however, substantially produced when H@sub 2@ or H@sub 2@O are used as additives due to the consumption of free fluorine by H, OH and H@sub 2@. The end products are dominated by COF@sub x@ with O@sub 2@ and by HF with H@sub 2@. The efficiency of PFC abatement (as measured by eV/molecule abated) decreases with increasing power and decreasing additive mole fraction. @FootnoteText@ @footnote 1@This work was supported by SRC and Applied Materials.

10:40am **MS+PS-ThM8 Modeling of Nonisothermal, Coupled Neutral/Plasma Dynamics in PFC Abatement Plasmas**, ***M.W. Kiehlbauch***, *A. Fiala, E.J. Tonnis, D.B. Graves,* University of California, Berkeley

Reducing PFC emissions is an area of increasing concern in semiconductor manufacture. One method of PFC emission reduction is through the use of point-of-use (POU) plasma abatement. In POU plasma abatement, an oxidizing species such as O@sub 2@ or H@sub 2@0 is added to the process tool effluent in the tool foreline. A plasma in the foreline is then used to convert PFCs to oxidized, wet-scrubbable species. Abatement plasmas can be used to reduce PFC emissions from oxide etch and in-situ CVD chamber clean processes and several commercial tools have been designed for these applications. Additionally, the abatement plasma structure is similar to downstream plasma sources which are increasingly used in chemical downstream etch and remote CVD chamber clean. A two-dimensional, coupled plasma and neutral model has been developed and applied to CF4/O2 and C2F6/O2 POU plasma abatement. The neutral model solves the overall neutral mass, momentum and energy balances. Additionally, the species mass balances are solved, together with a rigorous multi-component diffusion formulation. The neutral model is coupled via collisional terms to an INDUCT95 plasma model. The model allows the resolution of neutral temperature profiles and species concentration profiles. At high plasma powers, the neutral mean molecular weight decreases by ~ 50% while the neutral temperature increases by ~ 400%. The resulting density and velocity gradients have a major impact on the plasma structure and the composition of the gas flow leaving the plasma zone. We will present results that show these effects for various PFCs, power deposition profiles, flow rates, pressures and plasma powers. The relative importance of advective and diffusive transport will be considered. Additionally, the effect of wall temperature on the plasma structure will be investigated. Model results will be compared to those obtained experimentally. The application of these results to downstream plasma sources will be discussed.

11:00am **MS+PS-ThM9 Remote Plasma Sources for Cleaning CVD Reactors: Development and Implementation of a Technology for Green Manufacturing of Integrated Circuits**, ***S. Raoux***, *M. Sarfaty, T. Nowak, K.C. Lai, H.T. Nguyen, S. Thurwachter, J. Schoening, D. Silvetti, M. Barnes,* Applied Materials

The semiconductor industry is pursuing efforts to reduce emission of global warming PFC gases. Recently, a major advance in dielectric CVD (chemical vapor deposition) chamber cleaning has been introduced that virtually eliminates PFCs emissions from the process. Using NF@sub 3@ gas in a remote plasma source, the near complete dissociation of the gas achieves both superior chamber cleaning performance and improved environmental friendliness. In this paper, we will present experimental data (Mass and IR spectroscopy, Optical Emission Spectroscopy) used to identify the major

phenomena related to the destruction of NF3 molecules, the generation of reactive (F) species, the recombination of atomic fluorine into F2 molecules and the efficiency of (SiO2, SiN,...) deposition residue removal. We will review the design requirements for this Remote Clean@super TM@ technology with respect to environmental and process performance, manufacturability, integration to the CVD process tool, and energy efficiency. An environmental (EnV) analysis was conducted, based on a process architecture framework, manufacturing process modeling, and multi-dimensional characterization. The EnV analysis integrates ESH impacts, manufacturing costs, and process performance measurements into a larger systems view with dynamic process models, established business processes, and an upstream design approach. The analysis methodology is presented along with a case study to compare an in situ C2F6-based RF clean with the Remote Clean@super TM@ technology.

11:20am **MS+PS-ThM10 Study of NF@sub 3@-Based High Density Plasma Oxide Etch Processes for Reduced Global Warming Emissions**, ***L.C. Pruette***, *S.M. Karecki, R. Chatterjee, R. Reif,* Massachusetts Institute of Technology

Current oxide etch processes in the semiconductor industry rely on fluorocarbon chemistries, particularly perfluorocarbons (PFCs). The emission of PFCs from these processes has become a cause of concern to the industry because of the long atmospheric lifetimes and the suspected global warming properties of these molecules. Whereas it has been seen that the use of some fluorocarbon molecules in place of PFCs does lead to measurable emissions reductions, stemming typically from a more efficient breakdown in the plasma that that seen with PFCs, it is also known that any process based on a fluorocarbon source material, whether a PFC or not, is likely to emit significant quantities of CF@sub 4@, an extremely long-lived molecule possessing an appreciable global warming potential. The goal of the research presented here is to minimize the amount of CF@sub 4@ and other PFC by-products produced in high density plasma (HDP) oxide etch processes by replacing the fluorocarbon etch gas with an inorganic molecule, namely NF@sub 3@. The NF@sub 3@ gas acts as a fluorine source for the plasma, and is mixed with a rare gas diluent to enhance plasma stability. Experiments illustrating the etch behavior of this dilute NF@sub 3@ plasma with the addition of several different hydrocarbon additives meant to enhance photoresist selectivity and sidewall passivation, and scavenge free fluorine, will be discussed. Scanning electron micrographs (SEMs) will be shown to demonstrate process feasibility. In-situ optical emission spectroscopy data will be used to characterize the plasma, and quadrupole mass spectrometry (QMS) and Fourier-transform infrared (FTIR) spectroscopy data will be used to identify the global warming compounds and hazardous air pollutants (HAPs) found in the process effluent.

11:40am **MS+PS-ThM11 Environmentally Harmonized Silicon Oxide Selective Etching Process Employing Novel Radical Injection Technique**, ***K. Fujita***[1], *S. Kobayashi, M. Hori, T. Goto,* Nagoya University, Japan; *M. Ito,* Wakayama University, Japan

Dry etching of silicon oxide (SiO@sub 2@) films is an essential process for fabricating deep contact holes in ultra large-scale integrated circuits (ULSIs). This process has been developed by using high-density plasmas employing stable fluorocarbon feed gases such as CF@sub 4@, C@sub 4@F@sub 8@ and so on. Fluorocarbon gases, however, cause a serious environmental problem, namely global warming and hereby the production of fluorocarbon gases would be restricted. Recently, we proposed a novel radical injection technique using a fluorocarbon radical source replacing stable fluorocarbon feed gases for preventing global warming, where polytetrafluoroethylene (PTFE) is ablated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) such as reactive radicals are injected into the plasma reactor from externally. This technique, therefore, enables us to achieve a new plasma chemistry and a high-efficiency abatement due to the high exhaustion efficiency of reactive radicals coming from the plasma reactor compared with the stable gases. In this study, this system has been successfully applied to high-density plasma etching of SiO@sub 2@ over Si process and CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). A permanent magnet ECR plasma source which is very compact in size and easily scaled up to the large wafer size (~30 mm@phi@) was employed. The ECR zone was set about 6.5 cm above substrates. The Etching rate of SiO@sub 2@ and selectivity (SiO@sub 2@/Si) were 650 nm/min and 8, respectively at a microwave power of 400 W, a pressure of 6.5 Pa, a flow rate of 80 sccm and a bias voltage of -450 V in the ECR plasma employing the novel radical injection technique. These results indicate good characteristics compared with the conventional electromagnet ECR plasma. The etching mechanism are discussed on the basis of the behaviors of CF@sub x@ (x=1-3) radicals measured by the IRLAS.

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. Ramalingam***[2], *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 post-growth 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

[1] **PSTD Coburn-Winters Student Award Finalist**

[2] **PSTD Coburn-Winters Student Award Finalist**

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 hydrogen-depleted 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***[1]*, 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 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-to-hydrogen 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.

[1] **PSTD Coburn-Winters Student Award Finalist**

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.

Plasma Science and Technology Division
Room 612 - Session PS1-ThA

High Fidelity Pattern Transfer

Moderator: K.H.A. Bogart, Lucent Technologies

2:00pm **PS1-ThA1 High Fidelity Pattern Transfer**, ***K. Kasama***, *K. Yoshida, N. Ikezawa, T. Uchiyama,* NEC Corporation, Japan **INVITED**

The design rule of ULSI devices is being shrunk rapidly, now approaching to 150~130nm region. Moreover, the requirement of pattern formation fidelity, such as CD accuracy, overlay accuracy, pattern profile and so on, also becomes very strictly. For example, in the case of gate electrode formation, CD accuracy of less than ±10% is required after dry-etching, i.e., within ±15nm for 150nm devices. However, large CD fluctuation is usually generated in lithography process, and its amount reaches to CD budget. So, very tight CD control is necessary in dry-etching. In this presentation, current status of optical lithography will be introduced. Especially, we will discuss CD fluctuations induced by exposure tool stability, optical proximity effect and device topographic effect. In order to improve pattern fidelity, high NA scan exposure system, optical proximity effect correction mask and anti-reflective layer have been adopted as new lithographic techniques. Next, the resist pattern transfer by plasma process will be discussed, by mainly focusing on gate electrode formation. To suppress pattern density dependence (micro-loading effect) as well as gate oxide thickness reduction, we investigated two step etching process by using high density plasma, TCP. In a main etch step, vertical etched profile is formed under the plasma condition of high etch rate and low micro-loading, and then high selectivity etching to gate oxide is applied as a soft landing step. We have achieved good CD control of less than 10% in the 120~150nm gate formation. Moreover, we will mention about resist pattern shrinkage technique during BARC(bottom anti-reflective coating) plasma etching.

2:40pm **PS1-ThA3 High Volume Self Aligned Contact Etch for SRAM**, ***U. Raghuram***, *J.E. Nulty,* Cypress Semiconductor

Self-Aligned Contact (SAC) technology is used by Cypress Semiconductor in SRAM cells to form contacts which connect local interconnect and diffusion regions. SAC contacts allow designers to reduce the cell size by reducing the poly pitch. SAC technology is made feasible by the selective etch of the interconnect dielectric such as borophosphosilicate glass to the nitride etch-stop. This paper describes the key parameters for a manufacturable SAC etch, namely, gas chemistry, backside helium cooling, and total gas flow/ pressure. Polymer fill in the contacts provides the required selectivity to the etch-stop layer in SAC etch. The polymer profile is controlled by the sticking coefficient, which is controlled by the wafer temperature. Two common mechamisms for SAC etch are incomplete etch, 'grass', caused by excessive polymer deposition, and loss of selectivity, 'punch through', caused by insufficient polymer protection. Freon-23/ Freon 134a based chemistry provides self limiting nitride etch-stop performance. Uniform and constant wafer temperature is critical for process window in an etch controlled by polymer deposition. Using electrostatic chuck technology resulted in a wider process window with respect to backside helium control. The process runs at relatively higher pressures (50-100 mT) and total flows (70-150 sccm). Addition of argon allows the process to run at a moderate pressure and flow. It also improves the process uniformity. Backside helium setting of 8-12 Torr provides good wafer temperature control. The process was first developed for 0.5 micron design rules. The Cypress SAC process has been transferred to two different medium density plasma etcher platforms. This process has also been extended with minor modifications to etch SAC contacts for at least four SRAM technologies ranging from 0.5 to 0.21 micron design rules.

3:00pm **PS1-ThA4 High Density Plasma Oxide Etching of SAC (Self-Aligned Contact) and 0.25 micron HARC (High Aspect Ratio Contact) Structures: Process and Repeatability Results**, ***L. Marquez***, *B. Bosch, O. Turmel, S. Darcy, J.M. Cook,* Lam Research

A major challenge of SiO@sub2@ etching for sub-0.25 micron design rules is the stability of the process both long and short term. The very small, often deep, features together with the requirement for high selectivity guarantee that a very high degree of control of both the hardware and the process is essential. Stable SAC and HARC (> 10:1 aspect ratio) processes have been developed in an inductively coupled, high-density plasma dielectric etch tool. The repeatability of the processes was found to be dependent on the stability of the reactor's surface temperature, the material properties of the reactor's walls and the overall cleanliness of the chamber. The trends (etch rate, selectivity, uniformity, etc.) of the processes have been investigated in terms of power, pressure, flow, chemistry and wall temperatures. It is necessary to understand these trends in order to optimize the various process parameters such as selectivity and uniformity. The impact of surface temperature and material properties on the process results will also be discussed. Several marathons with both the SAC and HARC processes have demonstrated the manufacturability of both the processes and the high density plasma dielectric etch tool. The results of these marathons will be presented.

3:20pm **PS1-ThA5 The Angular Dependence of SiO@sub 2@, Si@sub 3@N@sub 4@, and Poly-Silicon Etching Rates in Inductively Coupled Fluorocarbon Plasmas**, ***C. Hedlund***, Uppsala University, Sweden, Usa; *F. Engelmark, H.-O. Blom,* Uppsala University, Sweden; *M. Schaepkens, G.S. Oehrlein,* State University of New York at Albany

Modern plasma etching processes, like self aligned contact (SAC) etching and the damascene and dual damascene dielectric etching, put new demands on the patterning processes. In the fabrication of self-aligned contacts, for instance, the silicon dioxide etching process has to stop on the curved silicon nitride spacer surface. At this curved surface a reduced SiO@sub 2@ to Si@sub 3@N@sub 4@ selectivity commonly is observed. In order to investigate the behavior of the angular dependence of the etch rate and the surface chemistry we prepared structures with a precise angle between the structure surface and the normal of the wafer surface by highly selective wet chemical etching of crystalline silicon. These micro machined structures consisting of either V-grooves or free standing rectangular mesas are ten times smaller than the plasma sheath, resulting in a ion flux normal to the wafer surface. The angular dependence of SiO@sub 2@, Si@sub 3@N@sub 4@, and Poly-Silicon etch rates have been studied in inductively coupled fluorocarbon plasmas. Our data indicate that the reason for the lower selectivity at inclined Si@sub 3@N@sub 4@ and poly-silicon surfaces is the angular dependence of the fluorocarbon film deposition and etching rates. At selective SiO@sub 2@ to Si@sub 3@N@sub 4@ conditions a relatively thin fluorocarbon film is formed on curved surfaces and corners as compared to planar surfaces. The surface chemistry and film thicknesses have been investigated with spectroscopic ellipsometry and. X-ray electron spetroscopy (XPS). The results will be presented along with SEM micrographs of etched structures.

3:40pm **PS1-ThA6 Process Optimization of Plasma Polymerized Resists for Advanced Lithography Applications**, ***O. Joubert***, CNET/CNRS, France; *C. Monget,* CNET France Telecom, France; *L. Vallier,* CNET France Telecom; *T.W. Weidman,* Applied Materials

CVD photoresist processes based on the plasma polymerisation of organosilane precursors such as methylsilane or dimethylsilane are currently investigated as a technique to extend 248 and 193 nm lithography. Upon exposure to UV light in air, these materials are oxidized generating areas which become more etch resistant to halogen based plasma than unexposed areas, providing a versatile approch to negative tone processes. Films have been deposited in a DXZ chamber from Applied Materials dedicated to dielectric deposition. Exposures have been performed using 248 nm (ASML /300) and 193 nm steppers (ASML /900 and Exitech microstepper). Film development was performed in high density plasma sources using mixtures of Cl@sub 2@, HBr and O@sub 2@. In all cases, developed CVD resist images are transferred through 500 nm of hard baked organic resist using SO@sub 2@/O@sub 2@ gas mixtures. This work reports the lithographic performance at 248 and 193 nm obtained with these dry resists (resolution down to 0.18 µm L/S at 248 nm and 0.13 µm L/S at 193 nm is achieved). Photosensitivity of the films, which can be tuned using the deposition parameters is strongly correlated to the film structure and density. In particular, FTIR analyses show that the photosensitivity increases with the methyl groups content, which favors an increase of the oxygen permeability in the film. The plasma development step is the most critical step of the process since the most serious issues in the dry lithographic process to achieve a good CD control across the wafer. Etch process parameters such as selectivity and uniformity are the more relevant parameters to control the final line width and profile before transfer into the underlaying organic layer. The performance and limitations of the all dry CVD process will be presented. @FootnoteText@ @footnote 1@ This work has been carried out within the GRESSI Consortium between CEA-LETI and France Telecom-CNET

4:00pm **PS1-ThA7 DUV Resist Degradation and Surface Roughening under Plasma Exposure**, ***W.H. Yan***, Microelectronic Division, IBM Corp.; *W. Moreau, R. Wise, Y. Cui,* IBM Corp.

This study investigate the plasma etch characteristic of several different types of DUV photoresist. It has been established that these photoresists suffer from degradation under exposure to common etch processes. We have demonstrated that resist degradation and surface roughening depend on resist polymer composition and etching process conditions. Results from this study clearly indicated: (1) Acrylate component in the polymer breakdown via chain scission during etching. That polymer breakdown causes resist surface pitting. (2) Ion bombardments, etch gas radicals, atoms and polymer deposition from etching reaction in the etching chamber further roughen the resist surface. (3) Heat and UV light in the etching chamber, on the other hand, crosslink resist polymer. The degree of crosslinking highly depends on resist polymer composition. We also investigated UV hardening, E-beam treatment as well as their impacts on resist etch resistance and surface roughening. Results showed that these treatments improve resist etch resistance, but not surface roughness. SEM and AFM were used to study resist surface and sidewall roughness. Gel Permeation Chromatography (GPC) was employed to analyze resist reaction under plasma exposure. The mechanism of resist roughness and its dependence on resist composition was discussed.

4:20pm **PS1-ThA8 Transfer Etching of Bilayer Resists in Oxygen-based Plasmas**, ***A.P. Mahorowala***, *K. Babich, Q. Lin, D.R. Medeiros, K. Petrillo, J. Simons, M. Angelopoulos,* IBM T.J. Watson Research Center; *G.W. Reynolds, J.W. Taylor,* University of Wisconsin, Madison

Thin film imaging offers the possibility of extending 248 nm lithography to sub-150 nm resolution. We have been working on a 248 nm bilayer resist scheme which utilizes a thin Si-containing resist on top of a thick, planarizing underlayer. The image is developed in the top layer and then transferred to the underlayer via an oxygen-based plasma etch. This paper will focus on two aspects of the critical transfer etch step - 1) etch resistance of the imaging resist and 2) control of profiles and resist roughening. The imaging resist thickness loss rate during the transfer etch is characterized by a rapid decrease in the first 10 seconds followed by a slow rate for the remaining etch. The relative importance of three phenomena occurring when Si-containing resists are exposed to oxygen-based plasmas - 1) oxidation of silicon, 2) deprotection of resist moieties, and 3) plasma etching of resist, will be discussed. FTIR studies on resist films indicate minimal film deprotection-related losses. XPS spectra show that the extent of surface oxidation increases initially and then becomes constant. Thus, this category of resists follows the model proposed by Watanabe and Ohnishi describing the etching of Si-containing resists as a combination of the oxidation of the silicon species and sputtering of the oxide-type layer formed. Post-transfer etch profiles using an oxygen plasma will be shown, and methods to reduce imaging layer resist faceting and thickness loss either by modifying the imaging layer silicon content or shifting to plasma chemistries causing sidewall passivation will be discussed. The effect of different etching chemistries and conditions on imaging layer roughening and striation formation on underlayer sidewalls will be explained with the aid of SEM micrographs and AFM images of etched feature sidewalls. The printing of 125 nm line/space patterns, and 150 nm trench features with 10:1 aspect ratios, in the underlayer will be demonstrated.

4:40pm **PS1-ThA9 Integration of Metal Masking and Etching for Deep Submicron Patterning**, ***C.T. Gabriel***, *R. Kim, D.C. Baker,* VLSI Technology

Although copper damascene interconnects offer many advantages over conventional subtractive etched Al alloys, the challenges and costs associated with converting to copper have combined to extend the useful life of Al alloy etching into the deep submicron regime. As a result, metal masking and etching are facing new challenges. DUV photolithography has replaced the conventional i-line technique for patterning fine metal pitches, but some DUV photoresists are less able to withstand the aggressive plasma environment than their i-line counterparts. Reflectivity increases at DUV wavelengths, so dielectric anti-reflective films are added on top of the metal stack. The mask-open process, where the dielectric film is plasma etched prior to etching the metal stack, alters the photoresist further and influences the subsequent metal etch. Aspect ratio dependent etch effects increase when etching narrow spaces resulting from tightened metal pitches, and gas additives may be required to protect the metal sidewalls. These effects are characterized and the challenges of deep submicron metal etch process development are discussed. The option of true hardmasked etching of the metal stack is also investigated.

5:00pm **PS1-ThA10 Manufacturable Aluminum RIE Processes for 150 nm and Beyond**, ***G. Stojakovic***, *X.J. Ning,* Siemens Microelectronics Inc. at IBM/Siemens/Toshiba DRAM Development Alliance; *E.W. Kiewra,* IBM Microelectronics at IBM/Siemens/Toshiba DRAM Development Alliance; *W. Kocon,* IBM Microelectronics

Three different aluminum etch processes - all proven to be manufacturable - have been developed for 150nm line/150space structures. The three schemes are: Organic ARC with photoresist as an etch mask, inorganic silicon oxynitride dielectric ARC (DARC) with photoresist as an etch mask, and a tungsten cap layer as a hard mask. The total metal stack height used in this work was 435 nm, with top and bottom Ti/TiN diffusion barriers. The designed aspect ratio of the wire for a 175 nm technology is 2.5, with a worst case of approximately 3.2. For 150 nm lines, this aspect ratio is substantially higher. For the two processes that use photo resist as the etch mask, the main task of the RIE process is to minimize the consumption of the resist during etch (i.e. maximize the etch selectivity of metal to resist). The metal etch tool used in this work was a commercially available plasma reactive ion etch system. The etch sequence starts with an ARC, DARC, or W hard mask open, followed by a Cl2/BCl3 based Al stack etch. An overetch is performed after a triggered end-point. Subsequent processing includes a down-stream H2O/oxygen plasma ash, followed by a water rinse. The key process parameters, such as gas flow rate, flow ratio of gases, and temperature that affect the metal profile and yield are discussed. It is shown that the RIE process can clear a sub-100 nm space for metal stacks having a height of over 400 nm. This indicates that aluminum RIE can be extended for even smaller structures. In the schemes that use photoresist as etch mask, the thickness of total metal stack is limited by the thickness of the photoresist. In the scheme that uses a PVD W hard mask, the total metal thickness is not a limiting factor for metal etch. The electrostatic chuck temperature plays a major role influencing metal profile and shorts yield.

Plasma Science and Technology Division
Room 609 - Session PS2-ThA

Pulsed Plasmas

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

2:00pm **PS2-ThA1 Power Modulated, Inductively-Coupled Plasmas**, ***M.V. Malyshev***, *V.M. Donnelly, J.I. Colonell, K.H.A. Bogart,* Bell Laboratories, Lucent Technologies; *S. Samukawa,* NEC Corporation, Japan **INVITED**

A review of plasma behavior in a power modulated (pulsed plasma) mode will be presented. Time dependencies of electron, positive ion, and negative ion densities as well as electron temperatures and electron energy distribution functions were measured with Langmuir probe, microwave interferometry, and TRG-OES in chlorine containing plasmas. Transition from an electropositive plasma to an ion-ion plasma in the afterglow of the pulsing period will be discussed. Formation of an ion-ion plasma is observed in higher pressure/lower power plasmas where Cl@sub 2@ is dissociated to a lesser degree and significant deinsities of negative ions can be produced through dissociative attachment of Cl@sub 2@. Anisotropic etching in inductively-coupled plasmas requires the use of bias and the effect of rf bias on the pulsed plasma mode of operation will be reviewed. In particular, the transition of the decaying plasma in the late afterglow into an RIE-type plasma during pulsed source and continuous bias operation will be shown and discussed. In this regime of operation, electron temperature sharply decreases in the beginning of the OFF cycle, goes through the minimum, and increases when the capacitive sheath near the wafer starts to heat electrons once the plasma density has decayed to RIE levels. Pulsed-power operation expands the boundaries of traditional plasma processing, and is a promising candidate for reducing plasma-induced damage and profile anomalies during plasma etching. Metal etching results in Lam 9600 TCP reactor show an 80% decrease of the severity of the device damage at an optimum condition of 50 µs ON and 50 µs OFF as compared to that of a continuous wave plasma. The use of power modulation for studying fundamental plasma dynamics will also be discussed.

2:40pm **PS2-ThA3 Method for Ion Energy and Ion Energy Distribution Functions Control at the Substrate during Plasma Processing**, ***S.-B. Wang***[1], *A.E. Wendt,* University of Wisconsin, Madison

A new method is proposed for control of ion energy and ion energy distribution functions (IEDF) at the substrate during plasma processing. In

[1] **PSTD Coburn-Winters Student Award Finalist**

contrast to the conventional approach of applying a sinusoidal voltage of variable amplitude and frequency to the substrate electrode, the new technique has a variety of advantages and provides a much greater degree of energy control by instead using a specially tailored waveform consisting of a periodic pulse or short high frequency burst in combination with a slow ramp. This rather adaptable technique for controlling the ion energy distribution function has important implications for selectivity and feature profile control in plasma etching, as well as film quality in plasma enhanced chemical vapor deposition (PECVD). In addition, it can be used to non-invasively measure the ion energy flux bombarding the substrate, and, therefore, can serve as a real-time indicator for etching process control and a real-time monitor for the drifting of plasma conditions during plasma processing. A time-dependent spherical-shell plasma fluid model is used to simulate different bias voltage waveforms and different area ratios for powered and grounded electrodes, and thus demonstrate the mechanisms of this method in producing a narrow IEDF of precisely controlled energy, independent of ion mass. Experiments in a helicon plasma using this method of substrate bias confirm predictions of sheath voltage evolution. Taking plasma noise into consideration, an IEDF with a single peak and full width at half maximum of 8 eV is expected for a 20 mTorr argon plasma, independent of the value of DC self-bias.

3:00pm **PS2-ThA4 Modulation Frequency Effects on Metal Etching Processes Using Pulsed-Power Plasma of Cl@sub 2@/BCl@sub 3@ Admixture**, ***C.J. Choi***, *O.S. Kwon, Y.S. Seol, I.H. Choi,* Hyundai Electronics Industries Co., Ltd., Korea

Using a langmuir probe and mass spectrometry, characteristics of pulsed-power plasmas of Cl@sub 2@/BCl@sub 3@ admixtures have been investigated for Al and TiN etching. From the measurements of ion energy distributions, kinetics of positive and negative ions were studied as a function of modulation frequency. Time-modulation was carried out in the range of modulation frequency from 1 kHz to 500 kHz for a 13.56 MHz radio frequency source. As the modulation frequency decreases, densities of the positive ions such as Cl@sub 2@@super +@ and BCl@sub 2@@super +@ and neutrals were not changed significantly. However, the negative ions of Cl@super -@ and Cl@sub 2@@super -@ increase greatly due to enhancement of electron attachment reactions since high-energy electrons larger than 5 eV were cooled effectively at low modulation frequencies, especially lower than 50 kHz. Etching characteristics for the metal films were also investigated as a function of modulation frequency. Etch rates of both Al and TiN films increased with decrease of the modulation frequency in the range of 1 kHz to 100 kHz. In particular, the Al etch rate at the lowest modulation frequency, 1 kHz, dominates over that in the continuous wave plasma at a fixed average power mode. By correlating the etching characteristics with the results from the plasma diagnostics, we determined the role of negative ions, generated predominantly during the plasma-off period, in metal etching with the pulsed-power plasma. Finally, the plasma charge-up on ferroelectric capacitor was examined after the metal etching with the pulsed-power plasma.

3:20pm **PS2-ThA5 Characterization of Process-Induced Charging Damage in Scaled-Down Devices and Reliability Improvement using Time-Modulated Plasma**, ***K. Noguchi***, *S. Samukawa, H. Ohtake, T. Mukai,* NEC Corporation, Japan **INVITED**

The charging damage from metal etching and dielectric etching was studied using MOS devices with gate oxide thickness of 1.9-6.0nm, and the impact of the plasma charging on reliability of scaled-down devices, as well as damage monitor methods appropriate for each plasma process and oxide thickness were investigated. Obtained results are as follows. For metal etching, in which electron shading effect is a major cause of charging, hot carrier effect dominated device degradation for oxide of 3.5-6.0nm. For thinner oxide (< 3.0nm), however, a gate leakage failure dominated but the failure rate decreased with gate oxide thinning below 3.0nm and became negligibly small below 2.2nm. For dielectric etching, the gate leakage current was an effective damage monitor, though high oxide electric field of >10 MV/cm was required to detect the latent damage effectively. Charge-to-breakdown or hot carrier degradation was less sensitive to the dielectric etching damage. Similar to the metal etching, the failure rate was lower for thinner oxide. Although the oxide damage seemed to decrease with device scaling, the problem may remain as latent damage or reduced reliability. To realize plasma process with low damage, time-modulated (TM) plasma technology was applied to the ECR metal etcher, the ultrahigh frequency (UHF) dielectric etcher, and the ICP polysilicon etcher. These etchers all showed reduction in charging damage compared to the conventional continuous-wave plasma. For example, the estimated amount of the charging current from the plasma was reduced to 1/4 in the metal etcher. The oxide yield improved by about 2 times in the dielectric etcher. The density of oxide traps created by the plasma process decreased in the polysilicon etcher. Thus, the use of the TM plasma is an effective and practical method to realize scaled-down MOS devices with better yield and reliability.

4:00pm **PS2-ThA7 Reduction and/or Elimination of Undesirable Topographic Differential Charging Effects in Semiconductor Processing by using Simultaneous Modulation of Source and Wafer RF**, ***N. Hershkowitz***, University of Wisconsin, Madison*; M.K. Harper,* Intel Corporation*; B.-W. Koo,* University of Wisconsin, Madison

High aspect ratio features are predicted to exhibit a variety of undesirable effects associated with electron shadowing and the resulting differential charging of dielectrics in semiconductor etching and deposition. Examples include notching in line and space structures, aspect ratio dependent etching, sidewall bowing, microtrenching and charging damage. In agreement with previous work, our experiments with Cl2 plasma etching of poly-Si and C2H2F4 of SiO2 (in a helicon etch tool) have found that modulation of the 13.56 MHz RF source can eliminate topographic charging effects in the absence of RF wafer bias, but fails in the presence of CW RF wafer bias. Data are presented showing that simultaneous source and wafer (on-off) modulation eliminates topograhic-charging effects while preserving the advantages of bias voltage. RF frequency and modulation duty cycle effects are discussed together with discharge mechanisms.

4:20pm **PS2-ThA8 Time-Resolved Optical Measurements of a Pulsed Inductively Coupled Plasma**, ***E.C. Benck***, *M. Edamura,* National Institute of Standards and Technology

Pulsed high density plasma sources have been suggested as an additional technique to alter plasma properties to help improve plasma etching. Time-resolved diode laser absorption spectroscopy has been used to measure the argon metastable densities in pulsed inductively coupled plasmas. These measurements were made in an inductively coupled version of the Gaseous Electronics Conference rf reference cell with Ar, Ar/O@sub 2@ and Ar/CF@sub 4@ discharges. These results are compared with time-resolved optical emission measurements from excited states of Ar, O and F atoms as well with time-resolved Langmuir probe measurements. Particular emphasis will be placed on the plasma behavior immediately after the turn on of the rf power to the coil and during the capacitive to inductive mode transition.

4:40pm **PS2-ThA9 Substrate and Plasma Heating within High Frequency Bi-polar Pulsed-DC Magnetron Sputtering Applications**, ***L.J. Mahoney***, *G.W. McDonough, D.C. Carter, G.A. Roche, H.V. Walde,* Advanced Energy Industries

Bipolar pulsed-DC power supplies have been developed and widely used for magnetron sputtering applications where periodic reversal of the sputter target polarity is used to suppress arc events. Pulsed-DC sputter deposition is particularly advantageous with reactive sputter deposition of oxides and select nitrides where arcs can lead to defects in deposited films and coatings. Recent technical advances now allow workers to widely adjust pulsed-DC operation by varying the pulse frequency up to 350 kHz and by varying the pulse-width or duty cycle. We have observed that at frequencies substantially greater than 100 kHz, the rate of change in substrate temperature substantially increases, a condition that can influence deposition processes. To better understand the mechanisms driving the increase in substrate heating, we examine the downstream sputter-deposition region of a closed-field magnetron with six inch diameter Al target by means of (1) fast-response thermal probes to measure the intrinsic power flux to grounded and floating substrates, (2) a time-resolved Langmuir probe to elucidate electron heating dynamics, and (3) analysis of the unique magnetron current and voltage waveforms. At pulsed-DC frequencies above 100 kHz, we observe that the intrinsic power flux density and electron density at the substrate both increase over DC and near DC sputter conditions. The measurements also indicate that the heating effect may be controlled by varying the pulsed-DC frequency and duty cycle. Moreover the heating effect correlates with transient features in the pulse-DC voltage waveform. From this work we infer that the mechanism for heating is likely to be driven by stochastic heating of the plasma electrons through a spatially-varying and time-dynamic sheath at the target, as analogous to conventional AC plasma sources. Potential process benefits of pulsed-DC operation at such high frequencies are also discussed.

Nanometer-scale Science and Technology Division
Room 611 - Session MS+PS-FrM

Diagnostics and Processes in Etching

Moderator: P.L.G. Ventzek, Motorola Inc.

8:20am **MS+PS-FrM1 Effect of CH@sub 3@F/C@sub 4@F@sub 8@ Ratio on the SiO@sub 2@-to-Si@sub 3@N@sub 4@ Selectivity in a Self-Aligned-Contact Etching Process for Giga-bit DRAM**, ***S.C. Park,*** Hyundai Electronics Industries Co. Ltd., Korea*; J.S. Kim,* Hyundai Electronics Industries Co. Ltd., Korea, South Korea*; J.J. Lee, K.T. Kim, D.D. Lee, Y.S. Seol, I.H. Choi,* Hyundai Electronics Industries Co. Ltd., Korea

Effect of CH@sub 3@F/C@sub 4@F@sub 8@ ratio on the SiO@sub 2@-to-Si@sub 3@N@sub 4@ selectivity in a self-aligned-contact(SAC) oxide etching process was investigated using an inductively coupled plasma. As published in other studies, the SiO@sub 2@-to-Si@sub 3@N@sub 4@ selectivity usually increases as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increases.@footnote 1@ However, we found out in this work that the selectivity gradually increases to a specific peak and sharply drops as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio continuously increases. Moreover, the selectivity was extremely poor at the valleys between the word lines (and in some cases, the nitride layer was even 'punched through'), while the selectivity was very high at the top shoulder of word line at a certain CH@sub 3@F/C@sub 4@F@sub 8@ ratio. It was found from the XPS and SEM analysis that the fluorocarbon film was built up without any bonding state change, as the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increased. The increase in the selectivity with increasing CH@sub 3@F/C@sub 4@F@sub 8@ ratio should be related with the amount of the fluorocarbon polymer deposition on the surface of Si@sub 3@N@sub 4@ barrier.@footnote 2@ However, the analysis of the fluorocarbon films could not completely explain the sharp drop in the selectivity and the extremely low selectivity at the valley between the word lines. Further studies showed that step coverage of the polymer film formed during the SAC oxide etching was very poor as the contact size decreased and the CH@sub 3@F/C@sub 4@F@sub 8@ ratio increased. In this case, less amount of the fluorocarbon gases should enter the contact hole and less amount of fluorocarbon polymer should be deposited on the Si@sub 3@N@sub 4@ etch barrier. This will eventually result in the sudden drop in the selectivity. @FootnoteText@ @footnote 1@ Y. Iijima and H. Okano, Jpn. J. Appl. Phys, Vol. 36, 5498 (1997) @footnote 2@ N.R. Rueger and G.S. Oehrlein, J. Vac. Sci. Technol. A 15, 1881 (1997

8:40am **MS+PS-FrM2 Plasma Cleaning of Via Bottoms Following Dielectric Etching**, ***P.J. Matsuo,*** *M. Schaepkens, G.S. Oehrlein,* State University of New York at Albany

In plasma etching, aspect ratio effects have been well documented. However,the dependence of the necessary cleaning steps following the etch on feature geometry have not. Cleaning via bottoms following the dielectric etch step can be critical to achieving low resistance contacts in multi-layer metallization schemes. Reducing this resistance is a prerequisite for the proper electrical function of Cu/low-k dielectric wiring architecture. We have examined in-situ surface modifications of post-etch blanket surfaces of several materials (Si, Cu, TiN, Al), resulting from Ar and O@sub 2@ cleaning treatments, using ellipsometry and XPS. We also investigated the removal efficiency of fluorocarbon and oxide residues at via bottoms for realistic aspect ratio structures by measuring the removal rate of fluorocarbon films or oxide films during O@sub 2@ plasma and Ar sputter cleaning, respectively. Ion driven cleaning procedures such as oxide removal, do not show a significant dependence on feature aspect ratio. On blanket films, to vias with an aspect ratio of 3, Ar sputter rates of BPSG remain constant. The removal of fluorocarbon residues under high density O@sub 2@ plasma exposure is heavily dependent on the neutral flux and is reduced in accordance with geometrical shadowing offset by the constant ion component. We have also investigated the surface chemistry of the residues as a function of feature geometry and cleaning process parameters.

9:00am **MS+PS-FrM3 Molecular Dynamics Simulations of Fluorocarbon Films**, ***J. Tanaka,*** Hitachi, Ltd., Japan*; C.F. Abrams, D.B. Graves,* University of California, Berkeley

Fluorocarbon plasma processes are used for highly selective etch processes of SiO@sub 2@ with respect to Si, SiN or photoresist. During fluorocarbon plasma etching, it is known that fluorocarbon films form on the latter surfaces, protecting them from active etch species such as F atoms. Even on actively etched surfaces of SiO@sub 2@, thin fluorocarbon films have been detected. During etching, the fluorocarbon films are an active participant, and in order to optimize etch processes, understanding these films is important. However, the structure and mechanisms of fluorocarbon film formation are not well understood. The nature of fluorocarbon film structure and its role in etching depend on the neutral and ionic species that impact it from the plasma, as well as the underlying material. We have chosen to use molecular dynamics of fluorocarbon ions impacting a carbon surface as a first step in understanding this complex process. In order to use molecular dynamics, we have developed a new C-F intermolecular potential. Our potential was developed based on the reactive empirical bond order (REBO) potential, using a strategy originally developed for carbon-hydrogen interactions. (Brenner, Phys. Rev. B, Vol.42, pp.9458) Initially, we calculated the argon ion sputtering yield of carbon at 100eV, 300eV and 500eV. For this low energy region, TRIM simulator significantly underestimated the sputtering yields while the yields calculated by the MD simulation agreed well with experimental results. Next, we simulated CF, CF@sub 2@, and CF@sub 3@ ion impacts at 100eV and normal incidence onto an amorphous carbon surface. In all cases, the initial process was net fluorocarbon film deposition at low fluences. For CF@sub 2@ and CF@sub 3@ ions, the fluorocarbon film reached a steady state thickness after several hundred ion impacts. In this talk, we will present the simulated film composition profile and the species that chemically and physically sputter from the surface as a function of ion fluence for each of the three ions simulated. In addition, the angular dependence of both film composition profile and sputtering characteristics will be presented.

9:20am **MS+PS-FrM4 Plasma-Induced Roughening of Resist**, ***S. Halle,*** *W.H. Yan, W. Moreau,* IBM Microelectronics*; J. Wittmann, A. Gutmann,* Infineon Technologies

A severe etch-induced line edge roughness of the resist pattern transfer during dielectric mask open reactive ion plasma processes is increasingly becoming a major issue in semiconductor processing as resist stacks shrink below 700 nm with sub 200 nm lithography. The resulting patterned features are observed to have serrated or "scallop-like" sidewall surfaces which are typically translated from the remaining resist / ARC layer to the dielectric layers and into the silicon, in both device contact-type and active area line space features. The origin of this effect, which results in a roughening of the silicon sidewalls and may severely compromise the patterned feature integrity, is poorly understood. In this study, we show that etch process conditions which produce "scallop-like" distortions are associated with a high degree of resist surface roughness as observed by SEM and measured by AFM. The roughening of a blanket resist surface exposed to reactive ion plasma etching is associated with a large "grain" size in the xy plane and a high "pitting" frequency in the z (depth) axis. The pitting frequency on blanket wafers is found to be qualitatively equivalent to the line edge roughness on patterned features. The extent of roughness is found to be highly sensitive to changes in etch process conditions such as bias voltage, chamber pressure, and gas flow constituents. The resist surface roughness, is examined under the following process conditions: argon sputtering only, fluorocarbon etching with low polymerization, fluorocarbon etching with a higher degree of polymerization. The contribution of the sputter component is found to be dominant; however, polymerizing fluorocarbon chemistry can also modulate the roughness. A qualitative model to explain the formation of the "scallop-like" features will be discussed.

9:40am **MS+PS-FrM5 Measurement of Residual Fluorine in a Polysilicon Etch Reactor with Fourier Transform Infrared Spectroscopy (FTIR)**, ***J.E. Daugherty,*** *E. Edelberg, V. Vahedi, A. Perry, J. Huang, R. Marsh,* Lam Research Corporation

One challenge in sub-0.18 µm gate etching is maintaining the integrity of the thin (<25 Å) gate oxide. This task is especially difficult for in situ hardmask applications where a dielectric (SiO@sub 2@ or Si@sub 3@N@sub 4@) hardmask is etched with a fluorine-containing gas (e.g., CF@sub 4@) in the same chamber that the underlying polysilicon gate is etched with Cl@sub 2@ and HBr. Fluorinated molecules can be released from in-chamber etch residues for several minutes after the fluorine-containing etchant is turned off, and free fluorine is produced when the plasma subsequently dissociates these compounds. If there is sufficient fluorine remaining in the chamber after the polysilicon is etched, it can reduce the selectivity to the underlying gate oxide. A similar reduction of the gate oxide selectivity is often noticed immediately following a dry clean of the etching chamber (i.e., a plasma clean). Since the chamber is cleaned with SF@sub 6@ or NF@sub 3@ plasma, residual fluorine from the cleaning plasma sometimes reduces the amount of remaining gate oxide

on the first wafer processed after the clean. We have used Fourier transform infrared spectroscopy (FTIR) to measure the concentration of several fluorine-containing etch products (e.g., SiF@sub 4@, HF) during gate etching with Cl@sub 2@/HBr in an inductively coupled plasma reactor. We have verified that the etch rate of thermal SiO@sub 2@ in Cl@sub 2@/HBr mixtures increases with increasing concentration of residual fluorinated etch products in the effluent of the reactor. We also observe that for in situ hardmask etching, the amount of fluorine-containing etch product that is observed at the end of the polysilicon etch step depends on the duration of fluorine exposure during the hardmask etch step.

10:00am **MS+PS-FrM6 Effect of W Reaction Byproducts on W/poly-Si Stack Gate Etching Process**, ***H. Morioka***, *M. Nakaishi, N. Abe,* Fujitsu Limited, Japan

W/(barrier layer)/poly Si stack is one of the most promising candidate for gate electrode structure of memory-embedded logic LSIs and DRAMs in the next generation because of low sheet resistance and compatibility with self-aligned contact (SAC) process, etc. Generally, the chemistry of W/poly Si stack gate etching is halogen-base, and most of W etching chemistry have higher etch rate of poly-Si than that of W itself. Although oxygen addition can increase the selectivity to poly Si above 1 by inhibiting Si etching, some troubles are still observed during poly Si etching step, such as non-uniform enhancement of etch rate, undercut profile, and serious RIE-lag. These facts make it difficult to achieve W/poly Si stack gate etching against very thin gate oxide. So, we examined the effect of W reaction byproducts on etching characteristics of other layers. Our experiments were performed on a high-density plasma (HDP) etcher whose plasma source could be operated in continuous mode or pulse modulated mode. We also compared fluorine-base chemistry with chlorine-base one to investigate the difference of etching byproducts. In this experiment, we found that W etching byproducts from a sample wafer and chamber wall enhanced the etch rate of poly-Si and SiO@sub 2@ especially for chlorine-base chemistry, and pulse modulation of plasma could reduce this enhancement. These facts suggest that W etching byproducts were decomposed into fragments in the plasma, these species were deposited on the sample surface and varied the etching characteristics. It is probable that pulse modulation reduced the dissociation of W reaction byproducts because of low electron temperature during afterglow.

10:20am **MS+PS-FrM7 Vacuum- and Near-Ultraviolet Spectra of Plasma Etching Discharges**, ***J.R. Woodworth***, *T.W. Hamilton, B.P. Aragon,* Sandia National Laboratories

We are measuring the absolute intensities of the Vacuum- and Near- UV emission spectra (24 eV to 4 eV) in metal etch and oxide etch plasmas in an inductively-driven Gaseous Electronics Conference reference cell. These spectra are of interest both because UV radiation may damage the circuits being processed and changes in the spectra may be used for process control. Spectra are being taken both in a cell with stainless steel electrodes and in a cell whose electrodes are covered with aluminum oxide, quartz and silicon to better simulate a commercial etch tool. In metal etch discharges containing mixtures of Cl2, BCl3, Ar, and N2, the vacuum ultraviolet spectrum above 8.8 eV is dominated by atomic Cl lines and Ar lines between 9 and 12 eV. Very little energy is emitted between 12 and 24 eV. The near ultraviolet spectra from 8.8 to 4 eV are dominated by B, BCl, Cl2, and etch products such as Si. Details of the experiments, effects of biasing the wafer, absolute line intensities and the effect of radiation trapping on the discharges will be discussed. This work was supported by the United States Department of Energy under Contract DE-AC04-94-AL85000. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Government

10:40am **MS+PS-FrM8 Etching of Organic Low Dielectric Constant Materials on the Lam Research 4520XLE**, *C. Janowiak,* ***S.L. Ellingboe***, *J. Flanner, I. Morey,* Lam Research Corporation

The low dielectric constant (k) of the polymeric materials SiLK and BCB have made them an attractive possible alternative to silicon dioxide as an intermetal dielectric in IC circuits. The lower dielectric constant is desirable to reduce capacitance and RC delay for higher chip speed, less cross talk, and lower power consumption. The forming of via and trench patterns in these low-k materials using a dry etch chemistry was investigated. Because SiLK and BCB is a polymeric material, oxygen is used as the primary etch gas, nitrogen as a dilulent and a hydrocarbon for sidewall passivation. Typically the organic low-k etch has a selectivity of low-k:PR ~1:1. Depending on the film structure, the PR can clear during the low-k etch, exposing the oxide hardmask for the latter portion of the etch. In the 4520XLE, this corresponds to a change in the etch process from a chemically dominated etch to an ion-dominated etch. Consequently, the plasma chemistry changes upon PR clearing and TEOS exposure, which can result in changes to etch rate, etch rate uniformity, and etch rate profile. Simulations of the SiLK etch results will be shown along with process results. The effects of process parameters such as RF power and oxygen-hydrocarbon ratio on etch performance will be discussed.

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

Emerging Plasma Applications

Moderator: W.M. Holber, Applied Science and Technology, Inc.

8:20am **PS-FrM1 Plasma Doping for Shallow Junctions**, ***S.B. Felch***, *M.J. Goeckner, Z. Fang,* Varian Semiconductor Equipment Associates; *G.C.-F. Yeap, D. Bang, M.-R. Lin,* AMD Inc. **INVITED**

This paper reviews the characteristics of ultra-shallow junctions produced by Plasma Doping (PLAD). PLAD is one of the alternate doping techniques being developed for sub-0.18 µm devices. In the PLAD process, the substrate is placed directly in a plasma that contains the desired dopant ions. A negative-bias pulse is used to drive the dopant ions from the plasma into the substrate. Here, we describe results from a wide range of experiments aimed at the production of ultra-shallow junctions for sub-0.18 µm devices. For the results shown here, a BF@sub 3@ plasma was used to provide the dopant ions that were driven into 200-mm Si substrates using wafer biases ranging from -0.14 to -5.0 kV. The ultra-shallow junctions formed with this technique hav e been examined with both SIMS and electrical profiling techniques. Good sheet resistance uniformity, charging performance, and added contamination levels have been obtained. When PLAD is used in the production of sub-0.2 µm gate length pMOSFETs, one finds sub-threshold swing, off-state leakage, and hot-carrier reliability similar to beamline-implanted ones. In addition, higher drive currents are seen in the plasma-doped devices. These results together with the expected small footprint and low cost-of-ownership of such a system make PLAD an attractive doping technique.

9:00am **PS-FrM3 Sputter-Wind Heating in Ionized Metal PVD@footnote 1@**, ***J. Lu***, *M.J. Kushner,* University of Illinois, Urbana

Ionized metal physical vapor deposition (IMPVD) is used to deposit seed layers and/or diffusion barriers in high aspect ratio trenches and vias for microelectronics fabrication. The physical sputtering is generated from a magnetron cathode. A secondary plasma is generated between the cathode and the substrate by an rf antenna. Experimental measurements suggest that sputter heating, generated by momentum and energy transfer from the sputtered metal atoms and the background gas atoms, rarifies the background gas and affects the transport of the sputtered atoms. In this study, sputter wind heating in IMPVD reactors is investigated using the Hybrid Plasma Equipment Model (HPEM) which has been improved to include processes relevant to sputter heating. These processes include ion energy-dependent yield, ion-energy dependent sputtered atom kinetic energy distribution, and heating due to the sputtered atoms. Improved algorithms have also been developed for electron transport in high magnetic fields to fully resolve the magnetron effect. The transport of the sputtered atoms is treated with a Monte-Carlo simulation. Statistics are collected on the interaction of sputtered atoms with the background gas, and are used to generate source terms in the continuity, momentum, and energy equations. Parametric studies have been performed for sputter heating in aluminum and copper IMPVD systems operating at low to high powers (up to 1500 W ICP, and 2000 W magnetron), and low to high reactor aspect ratio (height to radius) in 10's mTorr Ar. Due to the rarefaction in front of the target which results from sputter-wind heating, the slowing down length for sputtered atoms increases, thereby changing the flux of sputtered atoms to the substrate. Commensurate changes in the ion current to the target shift its I-V characteristics. @FootnoteText@ @footnote 1@This work was supported by SRC and TAZ.

9:20am **PS-FrM4 Opportunities and Challenges for Plasma Processes in MEMS Fabrication**, ***J.J. Sniegowski,*** Sandia National Laboratories **INVITED**

MicroElectroMechanical Systems (MEMS) are a burgeoning area of device development that has growing commercial applications in automotive, medical, and display technologies, with the promise of vigorous near-term expansion into areas such as information systems, chemical analysis, and consumer products. Microsystems present an arena for the emergence of

new plasma processing techniques, especially in the demanding area of etching. Today's most prevalent IC-based fabrication method is multilayer polysilicon surface micromachining. Plasma etch processes for defining structures in surface micromachined films comprise critical fabrication steps and must evolve to enable advances in microsystem capability. Typical plasma etch processes in surface micromachining will be outlined in terms of requirements like etch profile, aspect ratio, selectivity, and etch rate for several illustrative MEMS devices. Future etch demands such as submicron spaces with aspect ratios greater than 10, polysilicon films more than 6 microns thick, and large mask open areas will be described. In fact, the needs for vertical sidewalls and simultaneous clearing of both small (1 micron) and large (>10 microns) spaces, without any micromasking, already challenge conventional plasma tools and processes. Lastly, extremely deep silicon etching for very high aspect ratio structures, or through-wafer vias for material or optical transmission, interconnect, or environmental exposure will be discussed as perhaps the most difficult task for plasma etching technology. Although the time-multiplexed "Bosch" process has been viewed as a major breakthrough for the deep silicon etch application, opportunities remain for refinements, or alternatives employing more conventional etch tools.@footnote 1@ @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

10:00am **PS-FrM6 200 mm SCALPEL@super TM@ Mask Dry Etch Development**, ***G.R. Bogart***, *A. Kornblit,* Lucent Technologies*; I. Johnston,* Surface Technology Systems, UK*; A.E. Novembre, M.L. Peabody, C.S. Knurek, R.J. Kasica,* Lucent Technologies

SCALPEL (SCattering using Angular Limitation Projection E-beam Lithography) is based on the variation in scattering angles between two electron transparent materials supported on a membrane mask.@footnote 1@ Plasma etching of the membrane structure offers many advantages over wet etching using KOH. We have used a Time Multiplexed Deep Etching (TMDE) technique (Bosch process)@footnote 2,3@ for generation of large area thin (200:1 with a side wall angle of 89°. Etch uniformity is

10:20am **PS-FrM7 High Anisotropy Etching of 0.18 Micron Platinum Electrodes**, ***S.D. Athavale***, *D.E. Kotecki,* IBM, Microelectronics Division*; H. Shen,* Siemens*; J. Hwang, C. Ying, D.J. Lee, S. Mak,* Applied Materials, Inc.

Platinum is one of the most promising electrode materials for future high density DRAM capacitors based on high dielectric constant materials such as BST. Achieving veil-free, vertical sidewall profiles, when dry etching platinum, has remained an elusive goal due to the low volatility of etch-products under traditional plasma etching conditions. We have studied etching of platinum using a high-density plasma reactor equipped with a high temperature (>200°C) cathode. Statistical design of experiments (DOE) methodology was used. It has been found that the result of etching Pt is strongly influenced by the wafer temperature. For example, increasing the wafer temperature leads to a dramatic increase in the Pt etch rate and a change in resulting Pt profile. Nearly vertical sidewall profiles (89°) and veil-free Pt etching results are achieved on 0.18µm electrode. The key wafer-level issues and integration challenges associated with the etching of Pt electrodes under high temperature conditions are also discussed.

10:40am **PS-FrM8 Real Time Control of Plasma Tools During Recipe Changes and Transients@footnote 1@**, ***M.J. Kushner***, University of Illinois, Urbana*; S. Rauf,* Motorola Inc.

Successful development of real time control (RTC) of plasma tools should enable more rapid process development. A full etch process often includes multiple recipe changes to optimize, for example, break-through, main etch and over-etch. If the recipes are markedly different in gas composition or pressure, process parameters such as uniformity may significantly change during the transient. In the absence of RTC, maintaining desired process parameters requires changes in actuators based on interpolation between the beginning and end conditions. In this paper, the Virtual Plasma Equipment Model (VPEM) is used to investigate RTC strategies during recipe changes and transients. The VPEM is a "wrapper" for the Hybrid Plasma Equipment Model which contains simulated sensors, controllers and actuators. Recent improvements in the VPEM allow investigation of "real-time" (as opposed to run-to-run) control. Results from the VPEM will be discussed using response-surface based controllers to maintain process uniformity and rate during recipe changes for Cl@sub 2@ and C@sub 2@F@sub 6@ chemistries in ICP reactors. It was found that during recipe changes which, for example, significantly change mole fractions, the linearized response surfaces based on conditions at any given mole fraction are not adequate. Control is maintained for a portion of the transient but is eventually lost. To address this problem, real time mass spectrometer sensor data is used to interpolate between response surfaces which are the basis of (2 x 2) controllers. The response surfaces were generated using results from steady-state experiments. This strategy was able extend the dynamic range of control throughout the transient. @FootnoteText@ @footnote 1@This work was supported by AFOSR/DARPA, SRC and LAM Research.

11:00am **PS-FrM9 Plasma Injection with Small Helicon Sources**, ***F.F. Chen***, University of California, Los Angeles*; X. Jiang,* Broadcom, Inc.

Distributed plasma sources for large-area etching and deposition, comprising multiple helicon injectors, have been shown to be feasible.@footnote 1@ In this experiment, we studied the coverage provided by a single small source, varying the magnetic field and antenna configurations. The source was a 2.2 cm i.d., 12 cm long pyrex tube tightly covered by a thin, 3.9 cm i.d. solenoidal magnet coil providing up to a B = 100G field. A helical antenna was normally used to launch right-hand circularly polarized waves with 0-1000 W of 13.56 or 27.12 MHz power. The argon plasma was injected into to a 30 cm diam chamber with or without a permanent magnet "bucket". The low-field density peak@footnote 2@ usually found in helicon sources was not seen; instead, the maximum density almost always occurred at B = 0, as in ordinary ICPs. However, the densities were in the 10@super 11-12@ cm@super -3@ range characteristic of helicon sources. These were indeed helicon discharges, and the absence of a low-field peak was explained by detailed mapping of the magnetic field. With close-fitted solenoids, the plasma created near the edge of the source was scraped off by the entrance flange or was brought back to the top plate once the magnetic field became strong enough to entrain the electrons. At the higher fields, only the plasma created near the axis was available to a downstream probe. The high efficiency of helicon sources can be made available by properly designing the magnetic field coils so that all the field lines reach the interior of the downstream region and then diverge before striking the substrate. @FootnoteText@ @footnote 1@F.F. Chen and J.D. Evans, Proc. Plasma Etch Users Group (NCCAVS, 150 W. Iowa Ave., Suite 104, Sunnyvale, CA 94086) (1998). @footnote 2@F.F. Chen, J. Vac. Sci. Technol. A 10, 1389 (1992). .

11:20am **PS-FrM10 Ultra-Low-Temperature Formation of Silicon Nitride Gate Dielectric Films by Novel Plasma Technique**, ***M. Hori***, *H. Ohta, A. Nagashima,* Nagoya University, Japan*; M. Ito,* Wakayama University, Japan*; T. Goto,* Nagoya University, Japan

As device dimensions shrink below 100nm in ULSI, the thickness of gate dielectric film (SiO@sub2@) in FETs will fall to be 2-3nm range. The SiO@sub2@ film is replaced by a dielectric film with a higher dielectric constant film. In this study, we have successfully formed the ultra thin silicon nitride (SiN@subx@) films of 5nm in thickness at a low temperature of 300 degree C by the novel plasma technique using ECR SiH@sub4@/N@sub2@ plasma enhanced CVD (PECVD), where the charged species incident on the substrate were removed by two permanent magnets set above the substrate. It enabled us to form SiN@subx@ films by only neutral radicals. The experimental conditions were 0.5Pa, 300W, SiH@sub4@/N@sub2@ of 5/100sccm, and a substrate bias of floating. The films indicated the low leakage current of 7x10@super-8@A/cm@super2@ at 3MV/cm, dielectric constant of 7.3 and near stoichiometry composition. The reaction mechanism of film deposition with and without charged species were investigated by in-situ XPS and in-situ FT-IR reflection absorption spectroscopy. In the case of without charged species, two absorption bands ascribed to Si-N stretching mode at 970cm@super-1@ and 1085 cm@super-1@ were observed. The low frequency component is probably due to the metastable layer and the high one is due to the SiN@subx@ network. On the other hand,with charge species, the only low component was observed. The metastable layer is considered to cause the degradation of electrical properties of films. On the basis of these results, the control of ion bombardment on the growth was found to be a key factor for forming ultra thin SiN@subx@ films of high quality at a low temperature in PECVD.

11:40am **PS-FrM11 Characterizations of a Compact, Low-Field Toroidal Plasma Source for Downstream Plasma Processing**, ***X. Chen***, *W.M. Holber, D.K. Smith,* Applied Science and Technology, Inc.*; M.G. Blain, R.L. Jarecki,* Sandia National Laboratories

Activated atomic gases are used in semiconductor processing for applications including photoresist strip, passivation and chemical vapor deposition (CVD) chamber clean. We report the production of activated atomic fluorine, oxygen, nitrogen and hydrogen using a low-field toroidal (LFT@super TM@) downstream plasma source. The ASTRON@super TM@

reactive gas generator uses an electrodeless toroidal plasma source design, in which the rf power supply is integrated directly into the same enclosure as the plasma source. It operates at pressures from a few millitorr to one atmosphere. Typical plasma density is 3x10@super 13@ cm@super -3@. Thorough characterization of the plasma source is conducted using working gases such as NF@sub 3@, CF@sub 4@, CHF@sub 3@, C@sub 3@F@sub 8@, SF@sub 6@, O@sub 2@, N@sub 2@, NH@sub 3@ and H@sub 2@. The production and transport of the atomic species are investigated using chemiluminescent titration and etch rate measurements of silicon dioxide and photoresist. Greater than 90% of NF@sub 3@ is dissociated at flow rates of over 2 slm. The etch rates of SiO@sub 2@, SiN, WN, W and TiN are measured. Adding argon to an O@sub 2@/N@sub 2@ plasma increases the production of atomic oxygen and the rate of photoresist strip while not raising the power consumption. Contamination and particle measurements show that the plasma source is compatible with semiconductor processing. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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