### Monday Morning, October 2, 2000

### Plasma Science and Technology Room 311 - Session PS-MoM

### Plasma-Surface Interactions I

Moderator: E.R. Fisher, Colorado State University

#### 8:20am PS-MoM1 Plasma-Assisted Etching Processes for Dielectric Materials: Technological Challenges and Elementary Processes on Planar Surfaces and in Microstructures, G.S. Oehrlein, University of Maryland INVITED

Low pressure discharges are used for pattern transfer into dielectric layers in integrated circuit production, e.g. for etching of vias and trenches in the formation of multi-level interconnection schemes. The dielectric materials range from conventional SiO@sub 2@ and different spin-on glass films, organic insulators to porous materials. The control of plasma-surface interactions is a prerequisite for successful pattern transfer into the dielectric materials. We will review the challenges that exist for several prototypical pattern transfer applications, the dominant plasma-surface interaction mechanisms, and the technological solutions that have been demonstrated.

## 9:00am **PS-MoM3 Observation of Surface Reaction Layers formed in Highly Selective SiO@sub 2@ Etch Process, M. Matsui,** T. Tatsumi, M. Sekine, Association of Super-Advanced Electronics Technologies (ASET), Japan

We characterized the surface reaction layers formed by a fluorocarbon plasma for SiO@sub 2@ selective etching over Si and Si@sub 3@N@sub 4@, in order to understand the etch mechanism and to develop a process and tool for future ULSI processing. Specimens were etched using C@sub 4@F@sub 8@/Ar/O@sub 2@ plasma in a dual-frequency (27/0.8MHz) parallel-plate RIE system. The relationship between ion energy (assumed to be equal to peak to peak voltage (V@sub pp@) of rf bais) and the thickness and composition of the surface reaction layers were quantitatively analyzed using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The CF polymer layer and the SiF@sub x@O@sub y@ layer on the substrates were observed. We found that the etch rate is strongly affected by the ion energy and the thickness of the CF film on etched materials. In a highly selective etch process, the thickness of the CF layer on the SiO@sub 2@ surface is below 1 nm, while those on the Si@sub 3@N@sub 4@ and Si substrates are about 5-6 nm. The difference in the CF layer thickness on each material should be an origin of the selectivity. Both TEM and XPS observations revealed that reaction layers (2-4 nm) were formed at the interface between the CF layer and Si, Si@sub 3@N@sub 4@. The XPS analysis showed the composition of the reaction layer was SiF@sub x@O@sub y@. This SiF@sub x@O@sub y@ layers were thicker when the ion energy was high and the CF film was thin, i.e. a high etch rate condition for Si and Si@sub 3@N@sub 4@. SiF@sub x@O@sub y@ is thought to be an intermediary product of the Si@sub 3@N@sub 4@ and Si etching. In a highly selective etch process, CF film are so thin that ion energy is not reduced when ions pass through the film on SiO@sub 2@. On the other hand, at the surface of Si@sub 3@N@sub 4@ and Si, thicker CF film were formed and reduced the etch rate, resulted in thin SiF@sub x@O@sub y@ layer formation. @FootnoteText@ This work was supported by NEDO.

# 9:20am PS-MoM4 Early-stage Modification of SiO@sub 2@ Surface in Fluorocarbon Plasma for Selective Etching Over Si, K. Ishikawa, M. Sekine, Association of Super-Advanced Electronics Technologies (ASET), Japan

To understand the surface reaction mechanism that governs SiO@sub 2@ etch performance, we studied the surface evolution, starting at the very beginning of the etching process. We also studied the way in which fluorocarbon (CF) polymer reaches a steady-state at a specific thickness. For this purpose, we prepared a modified GEC reference cell and optical apparatus for in-situ time-resolved infrared attenuated total reflection (IR-ATR) spectroscopy with a germanium (Ge) substrate. The SiO@sub 2@ film was formed by plasma oxidation of Si sputtered on a Ge substrate. We made the SiO@sub 2@ film about 10 nm thick because, according to Fresnel's formula, the CF peak height is linearly proportional to CF film thickness when the underlying SiO@sub 2@ is less than a few hundred nm thick. While the SiO@sub 2@ film was being etched in Ar-diluted C@sub 4@F@sub 8@ plasma, we took spectra every two seconds. A peak, located at 1230 cm@super -1@, due to C-F stretching absorption and a trough, at about 1100 cm@super -1@, due to Si-O stretching absorption, were observed. Observations proved difficult due to an overlap between the two

components. By decomposing the spectra, we obtained the separated intensities of the CF and SiO@sub 2@ films. The time-dependence observations were fitted to a model, which enabled us identify the factors that enhance and inhibit CF film growth during SiO@sub 2@ etching. @FootnoteText@ This work was supported by NEDO.

#### 9:40am PS-MoM5 Silicon Etch Yields and Etching Chemistry in F@sub 2@, Cl@sub 2@, Br@sub 2@, and HBr High Density Plasmas, S.A. Vitale<sup>1</sup>, H.H. Sawin, Massachusetts Institute of Technology

Etch yields of silicon in F@sub 2@, Cl@sub 2@, Br@sub 2@, and HBr high density plasmas have been measured as a function of ion bombardment energy, ion bombardment angle, and plasma composition. This information forms a database of experimental values needed for feature profile evolution modeling. For all plasma chemistries, the etch yield increases with the square root of ion energy. Pure Cl@sub 2@ and pure HBr plasmas have very similar etch yields. Silicon etch rates are lower in HBr plasmas than in Cl@sub 2@ plasmas due to lower ion fluxes, not lower etch yields. The dependence of the etch yield on ion bombardment angle is significantly different for Cl@sub 2@ and HBr plasmas. The etch yield in Cl@sub 2@ plasmas decreases rapidly for ion angles above 60° (measured form the surface normal), which results in significant ion scattering from the sidewalls, causing the sidewall bowing and microtrenching seen when patterning polysilicon with Cl@sub 2@ plasmas. The etch yield in HBr plasmas decreases more gradually with ion angle, resulting in less ion reflection from feature sidewalls and could explain the lack of sidewall bowing and microtrenching seen when patterning polysilicon with HBr plasmas. HBr plasmas have higher etch yields than Br@sub 2@ plasmas due to: 1) the higher volatility of SiH@sub x@Br@sub y@ products compared to SiBr@sub 4@, and 2) extra Si surface coverage by small H atoms. As the temperature of the silicon increases, the etch yield in HBr plasmas decreases, due to reduced surface coverage by adsorbed Br and H atoms.

#### 10:00am **PS-MoM6 Studies on SiF@sub x@ Radicals in Fluorosilane Plasmas Used for Silicon Etching and Deposition**, *K.L. Williams*, *E.R. Fisher*, Colorado State University

Fluorosilane plasmas have been used in the microelectronics industry for etching of Si/SiO@sub 2@ and for deposition of fluorinated silicon alloys, such as a-Si:H,F. Specifically, fluorinated a-Si films are used in the fabrication of solar cells, photoreceptors, and thin film transistors. In spite of high quality film production, there is still controversy over the mechanistic aspects of deposition processes. Moreover, fundamental chemical and physical information on plasma species such as SiF@sub x@ radicals is not available. The surface reactivity of SiF and SiF@sub 2@ radicals during plasma processing of silicon-containing substrates using the Imaging of Radicals Interacting with Surfaces (IRIS) technique is reported. The molecular beam sources are 100% SiF@sub 4@, 90/10 SiF@sub 4@/H@sub 2@, and 50/50 SiF@sub 4@/H@sub 2@ plasmas. SiF and SiF@sub 2@ have been studied as a function of applied rf power (20, 40, 80, and 170 W) in each of these plasma molecular beams. Initial reactivity measurements of SiF on a Si substrate demonstrate that applied rf power has a significant effect on SiF scatter, which ranges from S = 0.05 at 20 W to S = 0.70 at 170 W. A S < 1 indicates that there is surface loss of SiF. Several possible mechanisms exist which may explain surface loss of SiF . These possible mechanisms will be discussed along with IRIS results for both SiF@sub 2@ and SiF scatter. Furthermore, IRIS results can be correlated with data from film characterization by Fourier transform infrared spectroscopy (FTIR) and profilometry of films deposited under various plasma parameters (applied rf power and % H@sub 2@ addition).

# 10:20am PS-MoM7 Ion Energy Distributions at the RF-Biased Electrode in an Inductively-Driven Discharge, *I.C. Abraham*, *J.R. Woodworth*, *M.E. Riley*, *P.A. Miller*, Sandia National Laboratories

We report the energy distributions of ions striking an rf-biased electrode in discharges in an inductively-driven Gaseous Electronics Conference Reference cell. The rf-bias and inductive power supplies were phase locked to a 13.56 MHz oscillator. Using a mass-and-energy sensitive ion analyzer we examined the ion energy spectra for ions of a variety of masses in discharges containing mixtures of the noble gases Ar, Ne, and Xe. The ions were sampled thru a pinhole in the rf-biased lower electrode. Oscillations of the plasma potential and the rf-bias waveforms on the driven electrode were directly measured to compare to the ion energy spectra. The ion energy distributions, which had a single peak and a width of 3.5 eV (FWHM) when the electrode was not biased, split into double peaked

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distributions as rf-bias was applied to the electrode. Lighter ions consistently had larger splittings in their energy distributions, with the largest splittings being in rough agreement with the rf potential difference between the plasma and the biased electrode. The influence of ICP coil power, rf-bias power, and pressure were investigated. Measurements of plasma densities and temperatures as well as comparisons to model ion energy distributions will be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

#### 10:40am **PS-MoM8 The Influence of High Density Plasma on TiN Films Deposited by Ionized Physical Vapor Deposition**, *D. Mao, J.A. Hopwood, K. Tao*, 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.@footnote 1@ One promising method of fabricating high-aspect ratio vias is ionized physical vapor deposition(I-PVD). Titanium nitride films were prepared by I-PVD in a gas mixture of argon and nitrogen. To understand the deposition mechanisms, optical emission spectroscopy analysis, Langmuir probes, and quadrapole mass spectrometry(QMS) were utilized to characterize the plasma. From the results of QMS, the dissociation of N@sub 2@ is as high as 50% for low N@sub 2@ partial pressure(~1.5mtorr), but decreases to 15% at 3.5mtorr. The properties of the TiN@sub x@ films were investigated by Rutherford backscattering, scanning electron microscopy(SEM), stress measurement, and electrical resistivity measurement. The ability of I-PVD to deposit titanium nitride at the bottom of narrow, deep vias and trenches was characterized by cross sectional SEM. The resistivity was found to increase as the N@sub 2@ partial pressure increases. The stress was found to increase from 1 GPa to 7 GPa as the bias voltage changes from -20V to -50V. The effect of nitrogen on the degree of ionization of sputtered titanium will also be discussed. The effect of dissociation of nitrogen and ion density on the characteristics of the TiN@sub x@ film will be presented by comparison with standard sputtering. @FootnoteText@ @footnote 1@ J. Hopwood, 'Ionized physical vapor deposition of integrated circuit interconnects', J. Physics of Plasmas, Vol. 5, pp 1624 (1998)

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### Plasma Science and Technology Room 310 - Session PS1-MoA

### **Emerging Plasma Applications**

Moderator: V.A. Shamamian, Naval Research Laboratory

### 2:00pm PS1-MoA1 A Surface-Micromachined Miniature Inductively Coupled Plasma Generator, J.A. Hopwood, O. Minayeva, Y. Yin, Northeastern University INVITED

The design, fabrication, and characterization of a surface micromachined plasma generator are described. Although there are many applications for miniature plasma sources, this device is intended for electronic excitation of gas samples such that the presence of impurities and toxins may be detected using a micromachined optical emission spectrometer. The plasma is sustained without electrodes by inductively coupling a 450 MHz current into a region of low-pressure gas. The inductively coupled plasma source is surface micromachined on a glass substrate by electroplating a planar spiral inductor (5 mm in diameter) and two interdigitated capacitors. A plasma can be sustained in argon and air between 0.1 and 10 torr (13.3 Pa - 1333 Pa) and rf powers between 0.3 and 3 W. The argon ion density increases from 10@super 10@ to 10@super 11@ cm@super -3@ over this range of powers. The electron temperature decreases from 4 eV to 2 eV as the pressure increases from 0.1 to 1 torr. Network analysis of the plasma generator circuit shows that over 99% of the applied RF power can be absorbed by the device. Of this, @<=@50% is absorbed by the plasma and the remainder of the power is dissipated as ohmic heating. Scaling laws associated with the miniaturization of inductively coupled plasma sources will be discussed including the dependence of electron temperature on scaled chamber dimensions, the preferred frequency of operation, and rf power coupling efficiency.

#### 2:40pm PS1-MoA3 Physics of Hollow Cathode Magnetron (HCM) Plasma Source, K.F. Lai, Novellus Systems, Inc.

The hollow cathode magnetron (HCM) is a new type of high-density plasma device developed for ionized physical vapor deposition (I-PVD). A novel magnetic geometry provides the confining magnetic field to sustain a magnetron discharge within a cup-shaped hollow cathode and the means of ion extraction from the source to the substrate. The use of a "cusp mirror" to reflect most of the escaping electrons back into the hollow cathode cavity has allowed the HCM to achieve extremely high plasma density (10@super 12@ - 10@super 13@ cm@super -3@). The HCM source is highly scaleable and has been successfully implemented in sources ranging from 19 to over 380 mm in diameter. Although the HCM has proven to be a very successful I-PVD source, there is a lack of understanding about its detail working mechanisms. Recent progress in three dimensional electrical probe measurements together with plasma modeling have revealed a different physics picture from our previous belief. Strong radial electric field on the order of 400 V/m was measured inside the hollow cathode. In conjunction with the confining magnetic field, a large ExB drift current is established because of the magnetron effect. As a result of this current and the incomplete shielding of the cathode voltage, the measured plasma density profile inside the cathode is hollow and funnel-shaped. The density profile becomes Gaussian as the plasma emerges through the magnetic null. Unlike other downstream plasma sources where the plasma density near the source is much higher than that downstream, no significant difference in plasma density is observed for the HCM. With the exception of the plasma edge where the presence of an energetic electron tail was evident, the electron energy distribution (EEDF) was approximately Maxwellian. Despite more than two orders of magnitude variation in plasma density, the electron temperature profile is relative flat throughout the entire plasma.

#### 3:00pm PS1-MoA4 Ion-Ion Plasma Formation and Negative Ion Extraction, *S.K. Kanakasabapathy*<sup>1</sup>, *M.H. Khater, L.J. Overzet,* University of Texas, Dallas

Ion-ion plasmas are relatively electron-free, positive and negative ion only plasmas formed in the afterglow of Pulsed-power high electron affinity gas@footnote 1@ (Eg: Cl@sub 2@) discharges. They hold the potential to provide ambipolar fluxes of positive and negative ions that could reduce differential charging of high anisotropy structures which cause@footnote 2@ etch non-idealities. Time-resolved Langmuir probe and Microwave Interferometry measurements in a pulsed ICP discharge show that

electrons are guickly lost (~ 10's of µmsecs) to dissociative attachment after turning power off. Time-resolved mass spectrometry has correlated the vanishing of electrons and consequently the confining plasma potential to the incipience of a negative ion (Cl@super -@) surface flux. Parametric characterization of Pulsed Cl@sub 2@ discharges has indicated that low pressures (1 mTorr), high powers (300 W peak), mid duty ratios (50%) and low pulse frequency (500 Hz) maximize this negative ion flux. Langmuir probe ion density decay rate measurements have shown ion-ion recombination to be the dominant loss process. We observe reproducible alternating irradiations of positive (Cl@sub 2@@super +@) and negative (Cl@super -@) ions corresponding to the negative and positive half-cycles respectively when a low frequency (20 kHz) bias applied to the mass spectrometer pinhole. This bias is applied as a phase-locked burst that is synchronized with the formation of ion-ion plasmas. Parametric characterization of this novel extraction technique reveals a bi-modal frequency response of the Cl@super -@ surface flux. This presentation is based upon work supported by the NSF under Grant No. CTS-9713262. @FootnoteText@ @footnote 1@D. Smith, A.G. Dean and N.G. Adams, J. Appl. Phys. 7, 1944-1962(1974) @footnote 2@G.S. Hwang and K.P. Giapis, J. Appl. Phys. 81(8) 3433-3439(1997).

#### 3:20pm **PS1-MoA5 Large Area Plasma Processing System Based on Electron Beam Ionization**, *D. Leonhardt*, S.G. Walton, D.D. Blackwell, W.E. *Amatucci, D.P. Murphy, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

Electron beam ionization is both efficient at producing plasma and scalable to large area (square meters). The beam ionization process is also fairly independent gas composition, capable of producing low temperature plasma electrons in high densities. A 'Large Area Plasma Processing System' has been developed based on the beam ionization process, with the goal of modifying the surface properties of materials over large areas. The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2-5kV, ~ 10 mA/cm@super 2@ electrons injected into a neutral gas background (oxygen, nitrogen, argon, neon). Typical operating pressures range from 20-200 mtorr with beam-collimating magnetic fields strengths of 100-300 Gauss. Thus far, electron beams have been produced using pulsed (10-4000 ms pulse length, >50% duty cycle) and dc hollow cathode discharges in dielectric as well as conducting chambers. Temporally resolved plasma characteristics deduced from Langmuir probes, optical emission spectroscopy and microwave transmission measurements will be presented. Over large areas (2 cm x 60 cm x 60 cm), results show low electron temperature (T@sub e@ ~ 0.6 and 1.5 eV in molecular and noble gases, respectively) in a bulk diffusion-dominated plasma with densities ranging from 10@super 9@ to 10@super 12@ cm@super -3@. Temporally resolved plasma-to-surface fluxes (via mass spectrometry) and their energy distributions will be presented to give further insight into LAPPS for material processing applications. If time permits, additional photoresist ashing tests demonstrating anisotropic pattern transfer will be discussed, along with design improvements in the electron beam source. Additional details of in situ diagnostics in LAPPS will also be presented by co-authors.@footnote 1@ @FootnoteText@ S.G. Walton, D.D. Blackwell -NRL/NRC Postdoctoral Research Associates @footnote 1@ See other presentations by co-authors at this conference.

#### 3:40pm PS1-MoA6 New Development of Plasma Technology for Biomaterial Engineering, INVITED

1. Introduction There has recently been increasing interest in the applications of plasma processing in a variety of industrial fields. One of applications of organic plasma processing now in practical use is plasma treatment. One of the advantages of plasma treatment is the fact that it is surface limited (500-1000Å) so that only the surface properties can be changed without affecting the bulk properties. In view of the fact that surface reactions of plasma treatment are initiated by plasma-induced surface radicals, study of the resulting radicals is of utmost importance for understanding of the nature of plasma treatment. Thus, we have undertaken plasma-irradiation of a wide variety of polymers, synthetic and natural, and the radicals formed were studied by electron spin resonance(ESR) coupled with the aid of systematic computer simulations. On the basis of the findings from a series of such studies, we were able to develop several novel biomedical application works in the field of biomaterial engineering. In this contribution, our novel application works in drug engineering on plasma-irradiated organic polymers will be presented, which include (1) preparations of multilayered tablet applicable for drug delivery system(DDS) of sustained- and delayed-release. (2) fabrication of functionalized composite powders derived from plasma-irradiation onto powdered polymers followed by mechanical applications in the presence of

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powdered drugs under anaerobic conditions,(3) preparation of biocompatible biomedical polymer surface useful for cathetal, as well as overviews of ESR studies on plasma-induced radicals of a variety of organic polymers.

#### 4:20pm PS1-MoA8 Detection of Perfluorinated Compounds by Microplasma Optical Emission Spectroscopy, D.D. Hsu, D.B. Graves, University of California, Berkeley

Because of impending restrictions on the emission of perfluorinated compounds (PFCs) by the semiconductor and other industries, methods for monitoring PFC concentrations in exhaust streams will be necessary. Current methods, including Fourier transform infrared (FTIR) spectrometry and mass spectrometry, are relatively expensive and complicated. One option to detect PFCs in exhaust streams at atmospheric pressure is the use of optical emission spectroscopy (OES) from a microhollow cathode discharge (MHCD). These intense glow discharges can be stabilized at elevated pressures and therefore offer the opportunity to exploit OES under a relatively wide range of conditions. This technique presents an inexpensive and simple way to monitor PFC concentrations. The circular geometry of a microhollow cathode produces intense excitation and hence, a strong source for OES. In the results we will present, various concentrations of PFC in a diluent gas were flowed through an MHCD with a hole diameter of 200  $\mu$ m, and the optical emission was analyzed. A direct current of 8 mA and a voltage of 250 V were supplied to sustain the MHCD. Concentrations as low as 10 ppm C@sub 2@F@sub 6@ in argon at 700 Torr were detected by examining atomic carbon, atomic fluorine, and molecular C@sub 2@ spectra in the visible range. A linear relationship between PFC concentration and integrated emission intensity was found. The results suggest that fluorocarbon concentrations on the order of 1 ppm can be detected with this technique. Details of the experimental setup and the observed spectra of various PFC concentrations in different diluent gases will be discussed. In addition, the results obtained suggest that MHCD OES might be a powerful analytical tool for other species as well.

### Plasma Science and Technology Room 311 - Session PS2-MoA

#### **Plasma Etching of Conductors**

Moderator: A. Kornblit, Bell Laboratories, Lucent Technologies

2:00pm **PS2-MoA1 Gate Engineering for sub 50 nm CMOS Devices**, *J. Foucher*, CNRS/LTM, France; *G. Cunge*, CEA/LETI, France; *D. Fuard*, *R.L. Inglebert*, *L. Vallier*, *O. Joubert*, CNRS/LTM, France

In less than ten years, we will be approaching the limits of the CMOS technology with typical gate transistor length of less than 30 nm. In the past, gate etch processes have been optimised to provide perfectly straight sidewalls while maintaining the selectivity to the ultra-thin gate oxide (less than 2 nm). Recently, a new approach has been proposed in which the process is tuned to obtain a silicon-based gate whose dimension is smaller at the bottom than at the top of the gate (notched gate). This new approach opens up the possibility of making gates with dimensions smaller than the ultimate resolution of the lithography. In this paper we discuss the mechanisms involved in the fabrication of notched gate. Experiments have been conducted on a very powerful plasma etch system dedicated to advanced studies. It consists in a Decoupled Plasma Source (DPS) from Applied Materials modified to host in situ diagnostics such as UV-visible ellipsometry, mass spectrometry, fast injection Langmuir probe and X-ray photoelectron spectroscopy (XPS). Oxide masked a-si gates are etched using a modified etch recipe allowing a lateral erosion of silicon to be obtained at bottom of the gate. This can be achieved by tuning the thickness and composition of the passivation layer formed on the silicon sidewalls (sidewall passivation layer engineering). The robustness of the sidewall passivation layer is reinforced in the first part of the process while, on the other hand, plasma conditions are tuned in the second part of the process to suppress the passivation layer. In a last step, lateral erosion of the silicon sidewall is possible at the location where no passivation layer has been formed. XPS data of the passivation layer formed at the different process steps will be shown as well as some details on the control of the notch depth. Finally some results showing gate dimension in the 20 nm range will be shown.

2:20pm PS2-MoA2 Fabrication of 80 nm PN-poly/metal Gate on Ultra-thin 1.5 nm Oxynitride, K. Kinoshita, S. Saito, Y. Saito, M. Narihiro, M. Ueki, H. Wakabayashi, Y. Ochiai, T. Mogami, Y. Hayashi, NEC Corporation, Japan A PN-poly/metal gate is thought to be the promising technology to embedded LSIs beyond 0.13  $\mu$ m design rule. This paper describes about the 80 nm PN-poly/metal gate fabrication technique on ultra-thin 1.5 nm gate oxynitride. Mix & match resist pattern by a point-beam EB system (JEOL, JBX-9300FS) for sub-0.1 µm pattern, and a usual KrF lithography system for wider pattern were developed over CVD-SiO@sub 2@/W/barrier/PN-poly-Si/gate-oxynitride stack on "8 wafer. The resist mask was transferred to CVD-SiO@sub 2@ hard mask layer, and then the poly/metal stack etching were investigated with a single chamber of an ICP type etcher (AMAT, Silicon Etch Centura DPS). The use of N@sub 2@-rich N@sub 2@/SF@sub 6@/Ar gas system for W etching, and the use of HBr/Cl@sub 2@/O@sub 2@ gas system for TiN etching generated rectangular cross section. Then, the PN-Poly-Si layer was etched by HBr/O@sub 2@ gas system. There existed the important correlation between relative oxygen density change by an optical actinometry and the PN-poly-Si etching. As the O@sub 2@ flow increased, the oxygen density increased, and the local etching to the silicon substrate through the thin gate oxynitride effectively suppressed. However, the excess O@sub 2@ flow brought etching stop on P-poly-Si region. XPS analysis for the etched P-Si wafer showed that the thicker oxide formation on the P-Si wafer etched at the etching stop condition. These results indicated that the P-Si surface oxidation brought both the high etching selectivity and the etching stop. The thinner the gate oxynitride, the narrower the process margins. Finally, good device characteristics were achieved.

# 2:40pm PS2-MoA3 Etch Rate Enhancement and Surface Roughening during W/Poly Si Stack Gate Etching Process, H. Morioka, M. Nakaishi, T. Ishida, Fujitsu Limited, Japan

W/Poly Si stack structure is one of the most promising candidates for gate electrodes of ULSI in the next generation because of its low sheet resistance and compatibility with self-aligned contact process. But most etching processes of W/Poly Si stack gate have some distinctive problems closely related to W and W etching byproduct, such as non-uniform etch rate enhancement, serious RIE-lag, and profile anomalies. We examined the catalytic effect of W and W etching byproducts on W/Poly Si stack gate etching. Our experiments were performed on a high-density plasma etcher. The chemistry was halogen-base and oxygen was used as an additional gas, which is sometimes utilized for increasing W etching selectivity to poly Si by inhibiting Si etching. An etching sample was poly Si or SiO@sub 2@ wafer on which a W chip was attached in the center. The W chip, which was the only source of W and W etching byproduct, was etched together with the sample wafer in the reaction chamber. The etch rates were measured as a function of distance from the W chip, and the surface roughness was measured by AFM. In this experiment, we found that W and W etching byproducts enhanced the etch rate of poly-Si and SiO@sub 2@, and the enhancement depended on distance from the W chip. The etch rate was maximum near the W chip. Besides, AFM observation revealed the increase of etch pits along grain boundaries on etched poly Si surface, and the increase of roughness of etched SiO@sub 2@ surface when they were etched with the W chip. These facts suggest that W etching byproducts and their fragments decomposed in the plasma are deposited on the sample surface and vary the etching characteristics.

#### 3:00pm PS2-MoA4 A Drift of Selectivity Depending on Chamber Seasonings in a Poly-Si/Oxide Etching Process using Inductively Coupled Plasma, K. Miwa, Fujitsu VLSI Ltd., Japan; T. Mukai, M. Nakaishi, Fujitsu Ltd., Japan

Chamber seasonings after plasma cleanings are useful to stabilize reactor conditions. However, etch-selectivities of poly-Si to oxide with the same recipe were found to drift depending on seasoning methods. After bare-Si wafers were etched with an ICP of HBr/O2 as Si-seasoning, over-etch rates of oxides with the ICP slightly raised and decreased to stop as Si-seasoning time was longer. In cases of blanket-oxide wafers were etched as Oxideseasoning, over-etch rates of oxides hardly drifted. Over-etch rates of poly-Si were nearly constant after the Si-seasoning or the Oxide-seasoning. Consequently, the etch-selectivity of poly-Si to oxide drifted after the Siseasoning. Optical emission intensity of SiBr/He in the over-etch plasma increased with increase of Si-seasoning time. Over-etch rates of oxides also drifted as functions of O2 flow rate and Bias Power to the bottom electrode of the ICP-Etcher. The Deposition formed on the oxides during overetchings after the Si-seasoning were identified as sub-oxides of Si using Xray Photoelectron Spectroscopy (XPS). These results suggest that etch-rates of oxides are enhanced and decreased by etch-products such as SiBrx (x=1,

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2, 3) in the over-etching plasma derived from the deposition on the reactor wall. The deposition would be formed during the Si-seasoning. When SiBrx coverages of the oxide surface are smaller than saturated coverage, the over-etch rates of oxides would be enhanced due to formation of silicon-oxybromide assisted with incident ions toward the surface. In cases of SiBrx coverages are larger than saturated coverage, excess SiBrx react with Oxygen atoms in the plasma to deposit sub-oxides of Si on the oxide surface. The sub-oxides would inhibit or stop the over-etching of oxides.

### 3:20pm **PS2-MoA5 Novel Dry Etch Chemistries for Metals**, *A. Orland*, Auburn University; *R. Blumenthal*, Auburn University, usa

Magentic metals are the principle components of the read/write heads and magnetic media of the data storage industry and are even finding their way into semiconductor processing. Although "lift-off" techniques, ion milling and non-specific plasma etches have proven adequate for the fabrication today's devices. These methods are simply not capable of fabricating the structures that will be required for the next generation of devices. Many promising chemistries have failed when involatile products form instead of the desired volatile products. This is likely the case for the etching of Fe and Co with CO/NH@sub 3@, where the formation of low vapor pressure dimeric species, such as Fe@sub 2@CO@sub 9@ (as opposed to the high vapor pressure monomeric species, FeCO@sub 5@) may be responsible for the low etch rates that have been previously reported in literature. Modification of the CO/NH@sub 3@ chemistry with the addition of methane, acetone, and/or H@sub 2@ to the mixture will be reported. Addition of these species is intended to result in both methyl and acetyl substitutions on the metal, which are known to inhibit the formation of undesirable, non-volatile, dimeric metal complexes. Other results will include the investigation of new chemistries, such as cyclopentadienylcarbonyl- chemistries, which will explore entirely new classes of possible volatile metal products. In-situ monitoring with supersonic pulse, plasma sampling mass spectrometry will yield information about all chemical species (both monmeric and dimeric) in the plasma environment, hence, it will provide a basis for understanding the chemical mechanisms of both successful and unsuccessful new etch chemistries.

# 3:40pm PS2-MoA6 Experimental and Modeling Results for Process Scaling from 200 mm to 300 mm Wafers, *S.C. Siu*, *D. Cooperberg*, *V. Vahedi*, *R. Patrick*, Lam Research Corporation

As the wafer fabrication industry begins to move from 200 mm to 300 mm wafers, the need arises to transfer existing processes both to larger wafers and to larger process chambers. Transferring a 200 mm baseline process to a 300 mm chamber is not trivial, but it is critical for quick ramp up from development to production. For next generation process chambers that can handle both 200 mm and 300 mm wafers, such as those from Lam Research Corporation, process scaling to larger wafers is less complicated because the chamber is fixed, but there are still issues which need to be understood. A successful process transfer will result in enormous savings in time and resources that can be better used to fine tune processes for 300 mm wafers, instead of re-establishing a 300 mm baseline process. Zeroeth order scaling principles previously derived and published by Lieberman and Lichtenberg@footnote 1@ are examined in this paper, and their applicability to practical process scale up are determined. Plasma parameters important in conductor etching, such as ion density, radical concentration, and sheath potential, were measured in a Lam Research 200 mm etch chambers and compared with measurements made in the next generation 300 mm etch chambers. Preliminary results show good agreement between the scaling predictions and plasma measurements. Modeling results show that reactor scaling parameters are application dependent. Scaling parameters for ion dominated etching may differ from those in which etch rate and profile evolution are more dependent on radical concentrations (e.g. resist trim, aluminum etch in chlorine). Additionally, predictions for process scaling may be dependent on the relative importance of radical depletion mechanisms (e.g. wall effects). recombination, reaction, volume loss, pumping @FootnoteText@@footnote 1@M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, John Wiley & Sons, Inc. (New York, 1994), chapter 10.

#### 4:00pm **PS2-MoA7 Improving AI Etch Processing in a High Density Plasma Reactor with a Faraday Shield**, *D.A. Outka*, *S.C. Siu*, *N. Williams*, Lam Research Corp.

As etch geometries become smaller, the uniformity of the reactor environment becomes increasingly important in achieving consistent results within a wafer and from wafer-to-wafer. This study examines the addition of a Faraday shield (FS) to an HDP (high-density plasma) reactor to aid in achieving this goal. The effect of the FS on Al etching is examined with wafer-level, plasma, and electrical diagnostics. The FS is an electrostatic shield inserted between the RF coil and the plasma. With this shield there is approximately a 10% reduction in the Al and oxide etch rates depending upon the RF power. Langmuir probe measurements indicate that this reduction is due mainly to a decrease in the plasma density. Electrical measurements of the impedance of the load with a RF probe were also performed and the results compared with a circuit model. These results also indicate a reduced coupling between the RF coil and the plasma. Based upon these results the impact of adding a FS to a commercial etch tool in terms of wafer performance and productivity is discussed.

4:20pm **PS2-MoA8 Transfer Etch Profile Control for 248 nm Bilayer Thin Film Imaging, S. Halle,** R. Wise, J. Brown, IBM Microelectronics; O. Genz, Infineon Technologies Corporation; A. Thomas, T. Dyer, IBM Microelectronics; A.P. Mahorowala, M. Angelopoulos, IBM T.J. Watson Research Center; S. Johnston, Lam Research Corporation

The technique of bilayer thin film imaging and transfer etch is expected to play an important role for extending 248 nm lithographic patterning to 135 nm and below feature sizes. Previous studies have demonstrated the utility of an O@sub 2@/SO@sub 2@ process in a poly TCP reactor to anisotropically etch the patterned resist through a novolak-like underlayer selective to a Si-containing imaging layer. In this study, both the width and profile control over a range of aspect ratios of a bilayer transfer etch for a 135 nm contact-like deep trench (DT) mask level and a equal line-space (LS) mask printed over severe topography, are examined. Transfer etch studies show that both the profile and the width of the etched feature can be controlled by both the ratio of O@sub 2@/SO@sub 2@ and the bias voltage in the TCP reactor to produce a zero bias vertical profile. The linewidth of the etched feature can be tailored with a positive or negative slope by either decreasing or increasing the ratio of O@sub 2@/SO@sub 2@, respectively, or decreasing or increasing the bias voltage, respectively. As the aspect ratio of the underlayer etch is varied from 5 to 8 in the DT level or as the feature is over-etched by 30%, the linewidth of the etched feature is unchanged. As the lithographic alignment of the LS mask level is incrementally varied with respect to a recessed trench from a previously patterned DT level, the transfer etch can be examined to aspect ratios >10, resulting in a minimum effective width of approximately 25 nm However, at the highest aspect ratios, the trajectory of the transfer etch is observed to be shifted from normal incidence by as much as 45 degrees. Semiempirical models are used to examine the origin of the altered trajectory of the ions, by determining the relative contribution of ion shadowing from the geometric asymmetry of the transfer into the recess and of the charging effect from thin dielectric films along the sidewall.

#### 4:40pm PS2-MoA9 Conductor Stack Etching: Technology and Productivity, R.A. Gottscho, Lam Research Corporation INVITED

Conductor etching in the semiconductor industry includes front-end applications such as gate and shallow trench stacks as well as back-end interconnect structures. Future applications center around new materials for gate stacks, to accomodate decreasing voltages and dielectric thickness, and high-k dielectrics, to enable higher density and powerless storage. The technological requirements in gate stack etching center on within wafer critical dimension, CD, control; but, production considerations demand equal attention to wafer-to-wafer, lot-to-lot, and machine-to-machine CD uniformity. For within wafer CD uniformity, gas injection, pumping, plasma generation, and edge ring design all play important roles. However, the aspect ratio variations inherent in circuit design and doping variations within the stack or from stack-to-stack ultimately limit the process window. Waferless cleaning of the chamber and delivered power control provide effective means for minimizing CD variation during large volume production. To preserve the device integrity of ultra-thin gate oxides and maximize yield, novel pre-end-point detection is used with and highly selective over-etch processes. Shallow trench etching mechanisms appear identical to those governing gate stack etching, but by shifting the balance between etching and deposition, trench profiles can be tailored to meet demanding requirements for top rounding, bottom rounding, and sidewall-angle uniformity. In back-end etching, traditional trade-offs remain for resist mask stacks: vertical profiles without residues and charging damage. Hard mask metal etching offers wider process window but at higher cost. The primary focus in the back-end is output, to be gained by increased throughput and longer times between cleans. It is the latter that is driving innovative changes in reactor designs and materials.

### Plasma Science and Technology Room 311 - Session PS-TuM

#### **Modeling of Plasma Processes**

Moderator: D.J. Economou, University of Houston

# 8:20am PS-TuM1 Optimization of Plasma Processing for Manufacturing Using Fast Integrated Models, B.Y. Yu, T.P. Phung, S.S. Shankar, Intel Corporation

Plasma processes are widely used in semiconductor manufacturing and a better understanding of the underpinning plasma and chemical principles is essential for better equipment design and process control. The major problems encountered in the plasma reactor are the non-uniformity at the wafer-level, etch profile controllability, and contamination. A fast and physically based integrated simulation tool has been developed to provide validated simulations of plasma processes, chemical reactions, transport, and surface evolution. The tool is employed to aid in understanding the plasma etching as a function of equipment variables. The tool consists of (1) a three-dimensional multi-species transient plasma processing simulator with capabilities for predicting wafer-level etch rate and uniformity, (2) a feature-level model for surface topographic evolution, and (3) a multi-scale linker to self consistently connect physical quantities between the two length scales@footnote 1,2@ In addition, different advanced numerical techniques have been developed for simulating realistic systems with multiple gas and surface chemistry. The plasma simulator is demonstrated on unstructured three dimensional grids with transport of mass, momentum, and energy. We have employed the integrated simulator to study multiple process windows in two different processes such as plasma physical sputtering of oxide (inter-layer dielectric) and CF4-based oxide etching. Simulation results are compared with experiments. @FootnoteText@ @footnote 1@ S.T. Rodgers, K.F. Jensen, J of App. Phys, (1997) @footnote 2@ S.T. Rodgers, S. Shankar, U. Hansen, and K.F. Jensen, J of Appl. Phys (submitted, 1999)

### 8:40am PS-TuM2 Modeling Transport and Etch Chemistry in High Density

Plasmas, M.W. Kiehlbauch, D.B. Graves, University of California, Berkeley In high density plasmas there is a complex interplay between neutral transport, charged particle transport, and gas and surface chemistry. High rates of mass, momentum and energy plasma/neutral collisional interchanges lead to large neutral gradients. Additionally, the low flow rates of these systems combined with fast diffusion and surface reaction often lead to species velocities that are much larger than the overall convective velocity. This makes for a difficult numerical problem that requires a self-consistent treatment of non-Fickian diffusion, chemistry, neutral convection, and plasma/neutral collisions. A two-dimensional, coupled plasma and neutral simulation has been developed and applied to high density inductively coupled plasmas used in etching high-k materials, an emerging area of semiconductor technology. Potential candidates are typically metal oxides, e.g. ZnO@sub 2@, and are etched using chlorine chemistry. Etch products often have low volatility. Neutral transport and surface reaction are especially important for low volatility species, which must be efficiently removed from the reactor before they can redeposit on the wafer or reactor walls. Failure to do so results in a build-up of reaction products and can lead to a loading effect. We present results showing that neutral transport is dominated by diffusion induced by gas or surface chemistry, depending upon the operating regime. We show that neutral transport can be a key factor in determining etch performance. Finally, simulation results will be used to suggest operating strategies that will optimize the etch process and minimize the use of consumables such as power, coolant and feedgases.

# 9:00am PS-TuM3 Plasma Chemistry Model for Fluorocarbon Etching of SiO@sub 2@, P. Ho, J.E. Johannes, R.J. Buss, Sandia National Laboratories; E. Meeks, Reaction Design INVITED

Plasmas of C@sub 2@F@sub 6@, CHF@sub 3@ and other fluorocarbons are used to etch silicon dioxide layers in the fabrication of microelectronic devices. Computational modeling of these systems can accelerate the design and optimization of these commercially important processes and equipment. We have developed a detailed model of the gas-phase and surface chemistry occurring in the C@sub 2@F@sub 6@ plasma - SiO@sub 2@ system. Reaction rates were obtained from independent published cross section and chemical kinetic data, whenever possible, or are estimates based on data for related molecules. A wide variety of experimental data from several experimental reactors were used to develop and validate the chemical mechanism. We have attained good overall agreement with the set of blanket etch rates, electron densities, negative ion densities, neutral species densities (i.e. CF, CF@sub 2@ and SiF) and ion current density data available to us. The work described here is part of a larger project on plasma etching funded by SEMATECH, and the work at Sandia National Laboratories was done under CRADA No. 1082. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### 9:40am PS-TuM5 Sustaining Another Decade of Innovation in Plasma Equipment and Process Design: Needs and Challenges@footnote 1@, M.J. Kushner<sup>1</sup>, University of Illinois at Urbana-Champaign INVITED Plasma equipment and process design have matured from a largely empirical practice to a science based discipline during the past decade based, in part, on the improvement of our fundamental understanding of the dominant processes through application of diagnostics and modeling. Sustaining this innovation in equipment and process design through the next decade will be challenged by increasingly stringent demands for reliability, speed of development and increased functionality of tools. As the market for microelectronics trifurcates into high performance, but commodity components manufactured largely by foundries, select extreme performance silicon components, and non-silicon advanced logic and optoelectronics, the demands for equipment and process design will likely also be segmented. The role of non-traditional components, such as MEMS, adds an additional dimension of uncertainty. In this talk, the challenges which will need to be met to sustain innovation will be discussed, with emphasis on the role of diagnostics and modeling. @FootnoteText@ @footnote 1@Work supported by SRC, NSF, AMAT, LAM and DARPA/AFOSR.

#### 10:20am **PS-TuM7 Electron Transport and Power Deposition in Magnetically Enhanced Inductively Coupled Plasmas@footnote 1@**, *R.L. Kinder, M.J. Kushner*, University of Illinois at Urbana-Champaign

The ability to deposit power within the volume of the plasma in Magnetically Enhanced Inductively Coupled Plasmas (MEICP) strongly depends on the magnetic field strength and configuration. The coupling of electromagnetic fields to the plasma typically occurs through a weakly damped helicon wave that penetrates into the bulk plasma and an electrostatic wave (the TG-mode). The TG-mode may penetrate into the plasma at low magnetic fields but deposits most its power near the plasmasurface interface at high magnetic fields. Under select conditions, the phase velocity of the helicon wave is similar to the thermal velocities of electrons which enables power deposition through collisionless heating. To investigate these processes, the Hybrid Plasma Equipment Model (HPEM) was improved by including a full tensor conductivity and electrostatic source terms in solution of Maxwell's equations, and by including 3-d components of the electric field in the electron Monte Carlo Simulation to resolve electron energy distributions (EEDs). Plasma parameters, wave propagation and location of power deposition will be discussed for process relevant gases (e.g. Ar/Cl@sub 2@, Ar/CF@sub 4@) as a function of magnetic field strength, configuration, and power. In the absence of the TG mode, with increasing B-field, electric field propagation progressively follows B-field lines and significant power can be deposited downstream. The tails of the EEDs are enhanced in the downstream region indicating some amount of electron trapping. Volumetric power deposition is ultimately limited by damping of the TG mode and the helicon wavelength. Wave propagation can be suppressed in electronegative gas mixtures where the wavelength exceeds the chamber dimension. @FootnoteText@ @footnote 1@Work supported by LAM, AMAT, SRC, NSF and DARPA/AFOSR.

#### 10:40am **PS-TuM8 Surface Reaction Model for Etch-rate Calculations in SiO@sub 2@ Selective Etching, S. Kobayashi,** T. Tatsumi, M. Matsui, K.K. Kawashima, M. Sekine, Association of Super-Advanced Electronics Technologies (ASET), Japan

A surface reaction model was constructed to predict Si and SiO@sub 2@ etch rates in fluorocarbon plasma. This model is based on experimental results, obtained in a dual-frequency (27/0.8 MHz) parallel-plate RIE system@footnote 1@ that is widely used in manufacturing processes. Although it is not based on a first-principal calculation, we carefully tried to keep physical meanings in the calculation. At the first, we chose input parameters, such as ion energy, ion flux, incident flux of CF@sub x@ species, and oxygen atom flux measured by various in-situ diagnostics such

<sup>1</sup> Featured Speaker - Science and Technology in the 21st Century

as IRLAS, QMS, and OES. Then, the reaction probability between fluorine and Si or SiO@sub 2@, and the energy loss by a C-F polymer layer were estimated from the experimental data. Based on this model, a simulation program was coded. The calculation starts on the clear Si or SiO@sub 2@ surface. Using the parameter set such as C-F species flux, ion flux and energy, the C-F polymer thickness and the etched amount were alternately calculated because each value depends on each other. Therefore, the calculation is iteratively continued until the variation of the C-F polymer thickness becomes small enough. We performed the calculation and obtained the selectivity when varying the C@sub 4@F@sub 8@ and oxygen flow rates individually. A highly selective etch process could be predicted using the model calculation and discussed the best condition for the etching process using a calculation instead of a conventional experimental analysis. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999) 1562.

11:00am PS-TuM9 3D Monte-Carlo Simulation of SiO@sub 2@ Film Growth Combined with Gas-phase Kinetic Model of TEOS-O@sub 2@ Plasma, A. Rhallabi, P. Retho, A. Granier, A. Goullet, G. Turban, IMN University of Nantes, France

A gas phase kinetic model of TEOS-O@sub 2@ plasma mixture combined with 3D Monte-Carlo surface model is developed to predict the microscopic properties of SiO@sub 2@ film as a function of the plasma parameters. The gas phase kinetic model is based on the mass balance equations of reactive species diffusing toward the surface. The mass balance equations in the diffusion chamber of our helicon reactor only take into account the electron impact dissociation and ionization rates of both TEOS and oxygen. Indeed, the low pressure (1 - 10 mTorr) and high density plasma allow to neglect the gas phase molecular reaction rates because the mean free path of the reactive species is large. In these conditions, the formation of the TEOS fragments (SiR@sub n@(OH)@sub 4-n@ where n=1-3 and R is OC@sub 2@ H@sub 5@) containing at least one OH group is mainly due to the dissociation of the R group into OH group by electron impact. On the other hand, a 3D kinetic Monte-Carlo model is developed to study the SiO@sub 2@ film growth. The fluxes of the reactive species are determined from the gas phase kinetic model. The SiO@sub 2@ growth process is mainly ensured by reaction between silicon sites and reactive precursors SiR@sub n@ (OH) @sub 4-n@ leading to the formation of oxygen bridges and the elimination of water. The nucleation phase mechanism was introduced in the surface model and showed the role of the substrate surface energy on the SiO@sub 2@ film adherence. The effects of some plasma parameters such as the RF power and the oxygen percentage on the deposition rate and the microscopic structure of the film are analyzed.

#### 11:20am PS-TuM10 Integrated Ionized and Conventional PVD Process Analysis Comparisons, P. Ventzek, V. Arunachalam, S. Rauf, Motorola Inc.

Conventional physical vapor deposition (PVD) processes or variations on them are still prevalent as tools for thin film deposition and are often the process of choice when damage or cost of ownership issues are considered. Integrated equipment feature scale models are required to facilitate making the decision whether conventional processes or their variants can do the job of the more sophisticated IPVD tools. Integrated models (equipment to feature) exist for conventional PVD processes but it is rare that the plasma physics aspects of the models are folded into the analysis. Reasons for this include that the coupling the magnetron physics into the model is not easy and that reactive sputtering processes which are more often than not conventional PVD processes are themselves complex. First, we will describe the coupling of a phenomenological magnetron model with the Hybrid Plasma Equipment Model (University of Illinois). Then, this paper will compare the performance (equipment to feature) of generic IPVD and PVD tools. Performance is quantified in terms of ion and neutral angular and energy distribution functions, fluxes of species to the wafer/feature and resultant feature profile.

# 11:40am PS-TuM11 Modeling and Experimental Verification of a Ti/Nitrogen/Ar Ionized Physical Vapor Deposition Tool, K. Tao, D. Mao, J.A. Hopwood, Northeastern University

lonized physical vapor deposition (IPVD) is one method used to deposit TiN barrier layers by the semiconductor industry. Compared to conventional physical vapor deposition or sputtering, IPVD can achieve directional deposition of thin films into high-aspect-ratio features. Metal atoms sputtered from the target are ionized by high-density plasma and the metal ions are collimated to the substrate by the electric field in the plasma sheath. Although some work has been reported on TiN film deposition by IPVD,@footnote 1@ there is little understanding of the plasma

fundamentals of reactive sputter deposition using IPVD. In this work reactive IPVD is being studied both experimentally and through plasma modeling. A global model of Ti-Ar-N@sub 2@ plasma is developed to predict the densities of the main plasma species, e.g. ionized, excited and dissociated particles of Ti, Ar and nitrogen. For a given chamber length and diameter, absorbed power, total pressure and gas flow rates, the particle and energy balance equations are solved to determine the plasma species densities and the electron temperature. To verify the validity of the model we carried out plasma diagnostics that include mass spectroscopy, optical emission spectroscopy and Langmuir probes. The dissociation of nitrogen is used to benchmark the model. By altering the N surface recombination coefficient we model the transition between the "metallic" and "nitrided" target modes. Experimental data show that the surface recombination coefficient for N is nearly 100% when the target is in metal mode because the freshly deposited Ti on the chamber walls increases the N sticking ability. A comparison of the model with the measured nitrogen dissociation ratios implies that the N surface recombination coefficient decreases to approximately 25% in the nitride mode. @FootnoteText@ @footnote 1@ J. Forster, Ionized Physical Vapor Deposition, Thin Films vol. 27, 141 (Academic Press, San Diego, 2000).

### Incorporating Principles of Industrial Ecology Room 304 - Session IE-TuA

#### **Green Manufacturing**

Moderator: P.M. Beauchamp, Jet Propulsion Laboratory

#### 2:00pm IE-TuA1 Challenges in Bringing Green Manufacturing Technologies to the Clean Room Floor, S. Raoux, Applied Materials INVITED

The semiconductor industry is undertaking major research and development efforts to reduce the environmental impact of its manufacturing processes. In particular, technologies have been introduced to eliminate atmospheric emissions of global warming compounds, reduce solid waste and conserve energy and water resources. At each technology node, semiconductor fabrication processes are amenable to change, and implementation of sustainable manufacturing practices should be favored. However, the stringent requirements of the semiconductor fabrication process render the introduction of novel manufacturing techniques a challenge. In this talk, we present innovative concepts that have been developed and integrated within semiconductor fabrication tools. Emphasis is placed on point-of-use (POU) solutions and environmental engineering using plasma technologies. We review the requirements that must be met by green technologies to be integrated to a complex manufacturing environment. We also present arguments to demonstrate that environmentally benign manufacturing methods can be developed and implemented in an economically viable way.

#### 2:40pm IE-TuA3 Eliminating Perfluorocompound Gas Emissions from CVD Chamber Cleans, P.J. Maroulis, A.D. Johnson, W.R. Entley, Air Products and Chemicals, Inc. INVITED

Perfluorocompond (PFC) gases such as CF4, C2F6, and NF3 are used extensively in semiconductor manufacturing processes. The largest volume use for these gases is for chamber cleaning following chemical vapor deposition (CVD). PFCs have long atmospheric lifetimes and absorb strongly in the infrared region of the electromagnetic spectrum where the earth's atmosphere would otherwise be transparent. Because of their infrared absorbances and persistence, PFCs are suspected of contributing to global warming. Through the World Semiconductor Council (WSC) the global semiconductor industry has voluntarily committed to reduce its cumulative emissions of perfluorocompounds. For the U.S., Europe, and Japan, PFC emissions will be reduced to 90% of 1995 levels by 2010 with some companies announcing even more aggressive reduction targets. Based on industry growth projections, substantial reductions for individual processes will be necessary to achieve these targeted levels. Both process optimization of traditional C2F6 based in situ cleans and substitution of NF3 for C2F6 in situ cleans are effective strategies for reducing the environmental impact of installed CVD tools. For new CVD tools, the manufacturers of semiconductor process equipment have developed and introduced a new remote NF3 cleaning technology that essentially eliminates PFC emissions. The combination of these three strategies, optimization of traditional C2F6 based in situ cleans, the substitution of NF3 for C2F6 in in situ cleans, and the implementation of the remote clean technology, has effectively solved the semiconductor industry's PFC issue. This presentation will contain data demonstrating the effectiveness of these strategies. In essentially all cases, perfluorocompounds emissions have been reduced by 50% to >99%.

#### 3:20pm IE-TuA5 Meeting IBM's PFC Emission Goals: Using the IBM In Situ Dilute NF@sub 3@/He Plasma Clean in Production on the Applied Materials 200 mm P5000 Lamp-Heated CVD Toolset, *C.M. Hines*, IBM Microelectronics; *W.R. Entley, R.V. Pearce, A.D. Johnson,* Air Products and Chemicals, Inc.

The major use of perfluorocompounds (PFCs) in semiconductor manufacturing is for residue removal following thin film deposition in chemical vapor deposition (CVD) chambers. One promising strategy to reduce PFC emissions in CVD chambers is the use of alternative clean gases that have lower global warming potentials and inherently higher utilization efficiencies (the percentage of the PFC that is consumed during the clean process) than the traditionally used carbon based PFCs, CF@sub 4@ and C@sub 2@F@sub 6@. Using this strategy, IBM developed a one-step in situ dilute nitrogen trifluoride/helium (NF@sub 3@/He) clean to replace the process of record (POR) C@sub 2@F@sub 6@-based cleans used in their Applied Materials (AMAT) 200mm Precision 5000 lamp-heated (DxL) CVD chambers. Successful implementation of the dilute NF@sub 3@/He clean into production is considered key to IBM meeting its PFC reduction

goals. Using quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy the process emissions of IBM's POR C@sub 2@F@sub 6@-based cleans and the new one-step dilute NF@sub 3@/He clean following deposition of both phosphosilicate glass (PSG) and tetraethylorthosilicate (TEOS) oxide were quantified. For TEOS oxide deposition the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the clean by 99 % with respect to the POR C@sub 2@F@sub 6@ clean. For PSG deposition, the one-step dilute NF@sub 3@/He clean reduced the MMTCE value of the POR clean by 96 %. In addition, the onestep dilute NF@sub 3@/He clean significantly reduced the total combined volumetric emissions of F@sub 2@ and HF compared to the POR C@sub 2@F@sub 6@ cleans. This presentation will include an overview of the implementation of the NF@sub 3@/He clean, current production data including tool performance (particles, mean time between wetstrips, etc.), and clean time/emissions comparisons between the POR C@sub 2@F@sub 6@ cleans and the one-step NF@sub 3@/He clean.

#### 3:40pm IE-TuA6 Treatment of Wastes from Chemical Mechanical Polishing Operations, S. Raghavan, Y. Sun, J. Baygents, University of Arizona INVITED

Chemical mechanical planarization (CMP) of dielectrics and metals has emerged as one of the most important techniques used in the fabrication of integrated circuits. In this technique, dielectric and metal films are globally and locally planarized using particulate slurries made from submicron-sized alumina and silica particles. A multi platen CMP tool can typically process 40 wafers per hour at a slurry consumption of approximately 100 ml/min/wafer. The aforementioned tool, if integrated with a cleaner, will require two to three gallons per minute of DI water. The mixing of CMP waste with the post-CMP cleaning waste typically results in a waste stream that is a very dilute dispersion of solids containing approximately 500 to 5000 ppm solids. In the case of metal CMP, the waste is likely to contain metal ions, unreacted oxidant such as hydrogen peroxide, residual corrosion inhibitors and other additives that are present in the slurry. Wastes from copper CMP may contain anywhere between 10 and 40 ppm of dissolved copper, in the uncomplexed and complexed form. By the year 2002, chemical mechanical planarization processes are expected to account for thirty percent of water consumed in a fabrication facility. Because of this statistics, increasing pressure is put upon fabrication facilities to treat the CMP wastes and recycle the water. Additionally, environmental regulations at the local and national level demand that solids and copper ions be removed before disposal of the water to publicly owned treatment facilities. In this presentation, an overview of the CMP waste problem will be provided and various techniques available for the treatment of CMP wastes will be critically reviewed.

#### 4:20pm IE-TuA8 Advanced Chemicals for Semiconductor Processing, E.R. Sparks, W. Wojtczak, S.A. Fine, ATMI INVITED

Three of the challenges to semiconductor processing are shrinking dimensions, copper metallization, and low-k dielectric materials. These challenges have been successfully addressed with a new group of waterbased chemicals that fortuitously have very favorable properties. - As lithographic dimensions shrink, etching and other processing parameters become more stringent. The residues created from photoresist during these proceses often incorporate fluorocarbon residues, and silicon and metal oxides that are impossible to remove with traditional chemicals. -New processes using copper damascene metallization have additional constraints, as many traditional chemicals are not benign to copper. -Higher speed devices are attainable with low-k dielectric materials, but these materials have special chemical requirements. Advances have been made to meet all three of these requirements by formulating chemical mixtures that are more benign, both environmentally and regarding health issues, than previously possible. These blends are water-based, waterrinsable, and free of regulated solvents, i.e., "green". The resulting technology has a very favorable cost of ownership due to lower costs related to abatement and disposal, compared to more traditional solvent blends.

5:00pm **IE-TuA10** High Throughput Process for Photoresist Stripping and **Residual Polymer Removal in a Via Post-Etch Process**, *M. Boumerzoug*, *Q. Geng*, *H. Xu*, Ulvac Technologies Inc.; *S. Gu*, LSI Logic Corporation; *S. Goh*, Silterra (M) Sdn. Bhd.; *T. Meyer*, *J. Seaton*, LSI Logic Corporation

In fabricating advanced IC, a multi-level interconnect scheme is commonly used and plasma etch is applied to form metal lines and via holes. During the plasma etch, a sidewall polymer is formed to control the etch profile. After the etch, the sidewall polymer needs to be removed completely to

insure a good via contact resistance. Typically, a very aggressive amine based chemical solvent is needed to clean up the sidewall polymer. As the design rule shrinks and aggressive zero overplot of the metal line and via plug is used to minimize the die size, some degree of misalignment between via plug and metal lines is inevitable. Wet chemical based post etch cleaning starts to show problems for the misaligned via and metal because they may attack exposed Ti, W and Al. An advanced dry clean process has been developed for removing post etch polymer. In addition, the dry clean process offers a lower cost of ownership (COO) than the wet clean process and is much safer and environmentally friendly. This technology utilizes the combination of microwave downstream and nondamage ion assisted processes to strip chemically altered and damaged photoresist and clean residue according to the chemical composition of each layer. The ion-assisted process is also found useful in stripping the photoresist at high rate. After this dry process, no wet strippers are needed; thus, the high cost and environment and safety concern associated with chemicals can be eliminated. In some cases, this dry clean process becomes an enabling technology for avoiding Ti and W-plug attack occurring in the wet cleaning processes. Split lots of wafers, which have two layer metal, were processed by the all-dry processes and tested electrically. The via chain resistance, metal bridging yield, metal continuity and electrical CD are all equal or better than the control wafers which were processed by wet chemicals.

### Plasma Science and Technology Room 311 - Session PS2-TuA

#### **Plasma Diagnostics I**

Moderator: T. Tatsumi, Association of Super-Advanced Electronics Technologies (ASET)

### 2:00pm **PS2-TuA1 Effect of Xenon Dilution on Fluorocarbon Plasma Chemistry and Electron Distribution Function**, *H. Sugai*, *T. Ishijima*, *M. Ikeda*, Nagoya University, Japan

Two types of unmagnetized high-density fluorocarbon plasmas, ICP (inductively coupled plasma, 13.56 MHz) and SWP (surface wave plasma, 2.45 GHz), are produced and compared in an identical vessel under the same gas conditions (10 % C@sub 4@F@sub 8@ + 90 % Ar, total pressure 20 mTorr). The ion and radical compositions are measured by a quadrupole mass spectrometer. The measurements at the same electron density of 2.5 x 10@super 11@ cm@super -3@ reveal that the ICP is more strongly dissociated than the SWP, with the smaller ratio of CF@sub x@ radical density to F radical density. Such different plasma chemistry between the two plasmas is attributed to the difference in the electron distribution functions (EDFs) observed in the experiment. Namely, the ICP has the EDF close to Maxwellian with higher electron temperature while the SWP has a bi-Maxwellian type of EDF composed of a cold electron group (lower temperature T@sub ec@) and a hot electron group (higher temperature T@sub eh@). The bi-Maxwellian EDF might be formed by stochastic heating at the plasma resonance layer in the SWP. Furthermore, replacement of the argon buffer gas with xenon gives rise to dramatic changes in plasma properties as follows. First, the xenon dilution makes it possible to obtain the same electron density by a factor of five less discharge power. Second, the radical density ratio of CF@sub x@ to F is increased by an order of magnitude in the Xe dilution, compared with the Ar dilution. Thirdly, the EDF measurement showed the value of T@sub ec@ lower by a factor of 2/3 in case of the Xe dilution. Finally, a global model of particle balance based on the measured EDFs supports these observations.

#### 2:20pm PS2-TuA2 Comprehensive Measurements of Neutral and Ion Number Densities, Neutral Temperature, and EEDF in a CF@sub 4@ ICP, H. Singh, J.W. Coburn, D.B. Graves, University of California at Berkeley

We present comprehensive measurements of the neutral number densities, ion number densities, neutral temperature, and the electron energy distribution function in a CF4 inductively coupled plasma at pressures between 1 and 30 mTorr, and deposited powers between 150 and 550 W. High degrees of dissociation are observed at the lower pressures. We believe this is a result of the large electron temperature (5-9 eV) at the lower pressures. The measurements of all the dominant radical and stable neutral species using appearance potential mass spectrometry allows the estimation of the neutral temperature at the neutral sampling aperture. The neutral temperature is also estimated from the change in the number density of a trace amount of argon added to CF4 when the plasma is turned on. Neutral temperatures up to 925 K are measured at the sampling aperture. The increase in neutral temperature with power at a Turned on Metamatical and the sampling aperture.

constant pressure results in a decrease in the total neutral number density at a constant pressure. The electron temperature is sensitive to the neutral number density, especially at low densities. This leads to a significant increase in the electron temperature with power, resulting in the higher degrees of dissociation observed at low pressures. The number densities of radicals and their corresponding ions are generally strongly correlated in the plasma. We show evidence for a large surface loss coefficients for C and CF radicals.

#### 2:40pm PS2-TuA3 Planar Laser-Induced Fluorescence Investigation of Fluorocarbon Plasmas, K.L. Steffens, M.A. Sobolewski, National Institute of Standards and Technology INVITED

Fluorocarbon plasmas are extensively used in the semiconductor industry for etching and chamber-cleaning applications. The etching process involves a competition between substrate removal and deposition of a fluorocarbon polymer layer on the wafer surface. The CF@sub 2@ radical is thought to be a major participant in the formation of this polymer layer either directly or by forming gas phase precursors which deposit to form the layer. Thus, measurements of the CF@sub 2@ radical are crucial to the understanding of etching chemistries. In this work, the planar laser-induced fluorescence (PLIF) technique was used to measure two-dimensional images of CF@sub 2@ density in CF@sub 4@ and C@sub 2@F@sub 6@ plasmas in the capacitively-coupled Gaseous Electronics Conference rf Reference Cell. Measurements were made at 200 mTorr with power deposited in the plasma ranging from 30 to 150 W, both without a substrate and with a Si wafer present, in pure fluorocarbon and in oxygen/fluorocarbon mixtures. In addition to the PLIE images, we obtained broadband emission images, which indicate the regions where reactive species are formed in the gas phase, and measurements of the rf current and voltage at the electrodes. The spatial distribution of CF@sub 2@ is observed to go through a transition as power is increased, becoming more radially-uniform at higher powers. In addition, the presence of the wafer was found to have a strong effect on the CF@sub 2@ by both increasing the CF@sub 2@ density and affecting the spatial distribution. The addition of O@sub 2@ decreases the CF@sub 2@ density even in the presence of a wafer. Comparisons will also be made with previous studies in 100 - 1000 mTorr O@sub 2@/C@sub 2@F@sub 6@ and O@sub 2@/CF@sub 4@ chamber-cleaning plasmas. The results of this study will help to elucidate the role of CF@sub 2@ in fluorocarbon plasmas as well as provide data for development and validation of plasma simulations.

# 3:20pm PS2-TuA5 Determination of Electron Temperature, Fluorine Concentration, and Gas Temperature in Fluorocarbon/Argon Plasmas using Optical Emission Spectroscopy, *M. Schabel, V.M. Donnelly, A. Kornblit, W. Tai, F. Klemens,* Lucent Technologies, Bell Laboratories

Recent advances in the interpretation of optical emission spectra from plasmas has made it possible to measure parameters such as electron temperature (T@sub e@), relative electron density, and gas temperature (T@sub g@) with this nonintrusive technique. This allows for the characterization and real-time monitoring of plasmas under conditions where the use of Langmuir probes is difficult (i.e. deposition plasmas or in manufacturing). Here we discuss the application of several advanced optical emission techniques to characterize fluorocarbon/Ar plasmas in an Applied Materials IPS inductively-coupled reactor. We have employed trace rare gas optical emission spectroscopy (TRG-OES), optical actinometry, and N2 vibrational spectroscopy to determine T@sub e@, fluorine atom concentration, and T@sub g@ respectively. Two etching processes, containing mixtures of Ar, C@sub 2@F@sub 6@, and C@sub 4@F@sub 8@, were evaluated as a function of pressure (5-90 mTorr). In the case of TRG-OES and optical actinometry, a mixture containing equal parts of He, Ne, Ar, Kr, and Xe (~1% ea.) was added. Large partial pressures of Ar prevent its use in TRG-OES because of radiation trapping effects (only the Kr and Xe lines were used to determine T@sub e@). Above 40 mTorr, T@sub e@ is insensitive to variations in pressure, and is ~2.5 eV. Below 40 mTorr, T@sub e@ increases with a decrease in pressure to 7 eV at 5 mTorr. The relative fluorine concentration increases with pressure and with the fraction of fluorocarbon species in the gas. At 5 mTorr, T@sub g@ is ~1010 K. Finally, we evaluated the effect of replacing Ar in the process gas with He or Ne, thereby allowing for the emission of the added Ar to be included with the Kr and Xe lines for determining T@sub e@. The resulting change in the accuracy of T@sub e@ measured by TRG-OES will be discussed in addition to how the use of He or Ne affects T@sub e@ and the relative electron density.

3:40pm PS2-TuA6 Time-Resolved Measurements of Fluorocarbon Radical Concentrations during Pulsed Oxide Etching Plasmas, *T.M. Bauer, X. Wu,* University of New Mexico; *J.L. Cecchi,* University of New Mexico, US

We have measured the time evolution of the concentrations of the fluorocarbon radical precursors, CF@sub 2@ and CF, in pulsed plasmas using oxide etching chemistries. These measurements were performed in an inductively coupled plasma (ICP) reactor with a CHF3/Ar feedstock. We have explored a range of ICP powers of 300 to 900 W and a range of total pressure from 10 to 30 mTorr. The concentrations of CF@sub 2@ and CF, were measured with a wavelength-modulated diode laser spectroscopy system, modified to provide data with a time resolution of less than 0.3 ms. The pulse repetition rate and duty factor were varied to explore the full range of CF@sub 2@ CF and kinetics. Following the initiation of the plasma, [CF] increases in a nearly first-order manner. The behavior of [CF@sub 2@] is more complicated. Under pulsing conditions where [CF@sub 2@] remains nonzero for the entire period, there is an initial, very rapid (< 3 ms) decrease in [CF@sub 2@], indicating an enhanced loss, followed by a slower rise to equilibrium. After the termination of the plasma, [CF@sub 2@] shows a rapid increase, followed by an exponential decay. [CF] shows only an exponential decrease. The time constant for [CF@sub 2@] decay is in the range of 0.08-0.20 s, while the time constants for [CF] are more than a factor of ten smaller. Both time constants decrease with increasing pressure, and show a much smaller dependence on ICP power. We interpret our measurements with simple kinetic models and have extracted kinetic parameters during both the plasma pulse and after plasma termination.

#### 4:00pm PS2-TuA7 Development of an Instrument: Resonantly Enhanced Multiphoton Ionization of Radicals Detected Using Time of Flight Mass Spectrometry, W.C. Flory, K.L. Williams, E.R. Fisher, Colorado State University

Plasma deposition and etching mechanisms have been studied extensively in recent years due to the technological utility of low-temperature plasmas. Much remains to be done on a molecular level, however, before a complete understanding of the underlying chemistry is gained. To this end, we have designed and constructed a molecular beam apparatus employing resonantly enhanced multiphoton ionization (REMPI) to examine the production and reactivity of radical species in low temperature plasmas. This newly constructed plasma molecular beam apparatus builds on our past experiments employing laser-induced fluorescence (LIF) to study the surface reactivity of plasma radicals. The REMPI instrument has been employed to study SiF radicals produced in a SiF@sub 4@ plasma. The SiF radicals are detected using [2+1] REMPI combined with time of flight mass spectrometry (TOFMS). The absorption band from the (1,0) C@super"2@@SIGMA@@super+@ <-- X@super2@@PI@@sub1/2@ transition of the SiF molecule was monitored. Production of SiF in the plasma has been measured as a function of plasma parameters, including addition of H@sub2@ and O@sub2@, and applied rf power. In addition to results for SiF, comparisons will be made to fluorocarbon radicals (CF, CF@sub3@) and to other silicon-containing species (e.g. SiH@sub2@, SiH@sub3@). Preliminary results from these systems will be presented.

#### 4:20pm PS2-TuA8 Temperature and Distance Dependencies of Fluorocarbon Species Desorbed from Polymer Deposited Metal Surface in C@sub 4@F@sub 8@ Inductively Coupled Plasma, H.-H. Doh, University of Tokyo, Japan; T. Ichiki, Toyo University, Japan; Y. Tezuka, Y. Horiike, University of Tokyo, Japan

To investigate the interaction between chamber wall and fluorocarbon plasmas, various fluorocarbon species such as CF@sub x@ (x=1-3) and C@sub 2@F@sub 4@, C@sub 3@F@sub 5@ emitted from the polymer coated copper stage has been measured by in-situ in C@sub 4@F@sub 8@ inductively coupled plasma using quadrupole mass analyzer (QMA) for the temperature of the stage, the distance between the QMA orifice and the stage. The QMA and hot stage are installed around the center of the chamber and the temperature of chamber wall can be controlled with water cooling system. The copper stage is equipped with heating rod, externally forced nitrogen blowing and can be movable with the radial direction. When we measured the radical density at the distance between hot stage and the orifice over 10 mm at 10 mT of pressure and 500 W of RF power, the results did not show any effect from hot stage and the densities of CF, CF@sub 2@, CF@sub 3@ have an order of 10@super 13@/cm@super 3@, 10@super 13@/cm@super 3@, 10@super 12@/cm@super 3@ respectively. At the distance below 10 mm, however, all radical densities increase and the behavior of CF@sub 3@ radical shows the biggest change with the decrease of the distance. Next, at the distance of 3 mm, the change of radical density with the surface temperature from

50 to 300 ° C was investigated. The density of CF@sub 2@ and CF@sub 3@ decrease slightly up to 100 ° C and 170 ° C, respectively then increase continuously to 300 ° C. The CF@sub 3@ radical density changed also dramatically with the temperature. It goes up to 7x10@super 14@/cm@super 3@ at the surface temperature of 300 ° C. It suggests that the pressure or the number of density around the hot wall is high locally. The increased number of density is due to the emitted species from the hot wall and consists of CF@sub 3@ mostly. It is considered that the surface plays both roles of sink and source of radicals for its temperature and CF@sub 3@ radical is the dominant species emitted from the hot wall inferred from the results measured at 3 mm of the distance with the variation of the surface temperature.

4:40pm PS2-TuA9 C@sub x@H@sub y@ Radical Measurements using Cavity Ring Down Spectroscopy in a Remote Ar/C@sub 2@H@sub 2@ Plasma, M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands; K.Y. Letourneur, Eindhoven University of Technology, The Netherlands, Netherlands; M.G.H. Boogaarts, Eindhoven University of Technology, The Netherlands; D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands

The ground state densities of C@sub x@H@sub y@ (x = 1,2, y = 0, 1)radicals in a remote Ar-C@sub 2@H@sub 2@ plasma used for high rate deposition of hard hydrogenated amorphous carbon films (a-C:H, rates up to 500 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CRDS). Both C@sub 2@ and CH could be spectroscopically identified and measured as function of C@sub 2@H@sub 2@ gas flow admixture. From previous studies we deduced that the main dissociation products of C@sub 2@H@sub 2@ dissociation in our remote plasma is C@sub 2@H and H. In an attempt to measure the ground state density of C@sub 2@H we looked for a spectroscopic signature in the 260-280 nm region where Laser Induced Fluorescence measurements of ground state C@sub 2@H have been reported. No clear spectroscopic fingerprint of C@sub 2@H@sub 2@ could be measured although a clear broadband absorption is observed. The absence of a fingerprint of the C@sub 2@H radical could be due to the limited spectral resolution (0.7 cm@sup -1@) of the laser system used. Another plausible reason could be the hostile plasma environment (including formation of clusters) which influences the formation process of C@sub 2@H to such an extend (in terms of excitation of rovibrational and electronic states) that broadband absorption results. However, the broadband absorption measured as function of the C@sub 2@H@sub 2@ gas flow admixture shows trends we expect from the C@sub 2@H radical. In an attempt to resolve the problems faced we have designed an experiment in which we measure the C@sub 2@H radical using simultaneously threshold ionization mass spectrometry and cavity ring down spectroscopy. First results of these experiments will be presented.

#### 5:00pm **PS2-TuA10 Electron Energy Control in Large-Diameter Inductively Coupled Plasma for High Performance of Etching**, *T. Urayama*, *T. Tsurumi*, Tokai University, Japan; *Y. Horiike*, The University of Tokyo, Japan; *S. Fujii*, ADTEC Co., Ltd., Japan; *H. Shindo*, Tokai University, Japan

A method of electron energy control was studied in an inductively coupled plasma of a large diameter employing the multimode antenna, for high performance in device fabrication etching plasma processes. In etching plasmas, the electrons are prone to be excessively energetic in high density plasmas generated at low pressures. In SiO2/Si selective etching, for example, the high etching selectivity has been hardly realized under high etch rate, and this is understood as the radical density is too much low compared with the ion density. This happens eventually because the electron energy becomes too high at low pressures. The experiment was carried out in an inductively coupled plasma which was produced in a stainless-steel chamber of 350 mm in diameter by supplying the RF power of 13.56 MHz through the quartz window at one end. The electron energy could be reduced by changing the azimuthal mode of one-turn antenna from m=0 to m=2 with no notable change in electron density. The electron energy reduction was found higher in the higher mode and essential at low pressures by Langmuir probe measurement. These behaviors were also confirmed by optical emission spectroscopy. The method was extended to two-loop antenna with different diameters which enabled us to make the radial mode as well as the azimuthal mode. It was verified that these twoloop antenna with the modes could imporove the radial uniformity as well as the electron energy reduction, and a physical sputter etch rate of Si showed 5% radial uniformity in 12 ich area. It was concluded that the electron free path divided by the induction field reverse distance was the essential parameter in electron energy control.

### Plasma Science and Technology Room Exhibit Hall C & D - Session PS-TuP

#### **Poster Session**

#### **PS-TuP1 Frequency Effects to E - H Discharge Mode Transitions in Inductively Coupled Plasmas**, *M. Edamura*, Hitachi, Ltd., Japan; *E. Benck*, National Institute of Standards and Technology

Inductively coupled plasmas (ICPs) have been used for plasma processes because of their high density and low pressure operation. Recently relatively lower density plasmas are used for many etching processes because the newest semiconductor devices have very small structures. Especially when ICP etching reactors are driven at low power, the effect of E-discharge (capacitive coupled discharge) can not be neglected. There are a wide variety of ICP reactors and the characteristics of E-discharge strongly depends on the reactor design. In this work, frequency effects to ICPs and E - H discharge mode transitions in ICPs are examined by Langmuir probe measurement. An ICP modified GEC reference cell and the discharge frequencies of 6.28 MHz, 13.56 MHz and 20.0 MHz were used for the experiment. By increasing discharge power, plasmas jump to high density H-mode discharges from low density E-mode discharges at certain powers. Higher frequency makes the voltage of the coil and the E-mode density higher and thus the E-H mode transitions occur at lower power. On the other hand, higher frequency makes the density of H mode lower because contribution of E-discharge in H mode makes the efficiency of plasma generation lower. Electron energy distribution functions (EEDFs) of 20 MHz discharge shows a high energy tail around 7-15 eV caused by the Edischarge between the coil and the plasma. Once the E-discharge contribution was removed by inserting an electrostatic shield, significant difference of FEDEs was not observed at these three frequencies.

# PS-TuP2 Effect of Wafer Temperature on High Aspect Ratio Hardmask Etching, *S. Lee, Y.C. Tien, Y.D. Chang,* Winbond Electronics Corporation, Taiwan

Fluorocarbon-based chemistries were used to study the effect of wafer temperature on the etch of high aspect ratio hardmask composed of BSG and Si@sub 3@N@sub 4@ layers. It is found that etch stop can occur easily at high temperature. The rate of polymer deposition plays an important role in etch stop. The etching rates were found to be inversely proportional to the wafer temperature. Such a relation indicates a negative activation energy in hardmask etching using fluorocarbon plasma. It also implies that in hardmask etching, complicated gas-surface reactions, but not simple one-step reaction, are involved. Different wafer surface temperature can provide different degree of activation for etching reactions. It is also observed that etching rates are very sensitive to the chamber condition, as indicated by optical emission spectroscopy. Analysis of etching rate and emission intensity trends indicates that CF@sub x@ may contribute more than F does in the etch of BSG and Si@sub 3@N@sub 4@, since polymerrich etching chemistries were used. Reaction models are proposed to interpret the observed trends.

#### **PS-TuP3 Time Resolved Mass Spectrometric Plasma Diagnostics**, *G.J. Peter, G. Nicolussi,* Balzers Instruments, Liechtenstein; *N. Mueller,* Balzers Instruments, Liechtenstein, Principality of Liechtenstein

The energy distribution of the ions in a plasma is one of the most important process parameters. This distribution can be measured for different ion species by a combination of an electrostatic energy filter and a mass spectrometer (a Plasma Process Monitor PPM). Thus far, most of such investigations have been performed in plasmas under equilibrium conditions. On the other hand, little is known about the ion energy distribution during ignition of plasmas, i.e. in a non-equilibrium state. Furthermore, it has become a common technique to modulate deposition and cleaning plasmas by means of periodically changing magnetic and/or electric fields which as well results in non-equilibrium plasma conditions. Measurements of the transient ion energy distributions in such processes contribute to a deeper understanding of the mechanisms involved. This in turn, facilitates process development in order to avoid conditions that might result in electronic device damage (e.g. due to high energetic ions). Our investigation includes 3 different non-equilibrium plasmas: A DC-planar magnetron plasma during ignition, a magnetically modulated DC plasma, and a power modulated RF-plasma. The PPM utilized in these experiments is a combination of a differentially pumped specially adapted cylindrical mirror energy analyser and a quadrupole mass filter with mass ranges from 0 - 512 amu up to 0 - 2048 amu. An energy resolution of 0.3 eV and unit mass resolution over the whole mass range are achieved. To perform time resolved measurements the mass and energy filter are set to the desired values and data acquisition is made with a Multi-Channel Scaler (MCS).

#### PS-TuP4 The Boron Effects on YMnO@sub 3@ Thin Films Etching in High Density Ar/Cl@sub 2@/BCl@sub 3@ Plasma, B.J. Min, Chungang University, Korea; Y.T. Kim, KIST, Korea; C.-I. Kim, Chungang University, Korea

Ferroelectric materials, such as Pb(Zr,Ti)O@sub 3@ (PZT), SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT), (Ba,Sr)TiO@sub 3@ (BST), YMnO@sub 3@ have attracted much attention for use in nonvolatile memories. In particular, YMnO@sub 3@ thin films are excellent materials for high integrated ferroelectric random access memory (FRAM) with metalferroelectric-silicon field effect transistor (MFSFET) structure. Although etching processes for YMnO@sub 3@ thin films must be developed to fabricate MFSFET type FRAM, etching of YMnO@sub 3@ have not been reported. Thus, we studied the etching properties of YMnO@sub 3@ thin films using high density plasma. In this study, YMnO@sub 3@ thin films were etched with Ar/Cl@sub 2@/BCl@sub 3@ gas chemistries in inductively coupled plasma (ICP). Photoresist (PR) and SiO@sub 2@ were used as mask materials. Etching properties of YMnO@sub 3@ were measured according to the various etching parameters such as rf power, dc bias voltage, chamber pressure and gas mixing ratio. The trends in the effect on etch rate and selectivity to mask materials for BCl@sub 3@ ratio to Ar/Cl@sub 2@ have been determined. YMnO@sub 3@ was dominantly etched by Ar ion bombardment. Selectivity to PR and SiO@sub 2@ increased as decreasing mole fraction of Ar gas. Additive BCl@sub 3@ enhanced relative etch rate, selectivity and profile. Chemical reaction and residue of etched surface was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). As mole fraction of BCl@sub 3@ varied, boron effects with respect to residue were investigated by etched profile of SEM (scanning electron microscopy) image. In order to analyze the effect of radical density of Cl and ion current density in plasma of various gas chemistries, optical emission spectroscopy (OES) and single Langmuir probe were utilized. Change of stoichiometry on the etched surface is discussed by comparing with OES analysis.

#### PS-TuP5 The Study of Optical Emission Spectroscopy in SrBi@sub 2@Ta@sub 2@O@sub 9@ Etching Using Inductively Coupled Plasma, S.U. Shin, D.P. Kim, E.-G. Chang, C.-I. Kim, Chungang University, Korea

Recent developments in real-time optical emission spectroscopy (OES) for plasma diagnostics are critically mentioned. The OES results also suggest certain chemical reactions to take place in the plasma, which can be correlated to the chemical composition of the films. In this report, since the research of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) thin film etching was few(specially Cl@sub 2@-base ), we had studied the surface reaction of SBT thin films using the OES in high density plasma etching. Measurements were made as a function of input power, pressure, bias power, and as a function of gas ratio for Cl@sub 2@ and Ar. It had been found that this SBT etch rate appeared to be more affected by the physical sputtering between Ar ions and surface of the SBT compared to the chemical reaction in our previous papers. The change of Cl radical density measured by the OES as a function of gas combination showed the change of the SBT etch rates, therefore, chemical reactions between Cl radical in plasma and components of the SBT enhanced to increase the SBT etch rates. According to the OES spectra, Ar ion bombardment strongly effects to remove Sr, Bi, and Ta atoms, however, some of the Bi and Ta atoms react with Cl radicals and form a little of BiCl@sub x@ and TaCl@sub x@, respectively. The surface residues remaining after the etch were investigated using XPS and SIMS for all of the etch conditions used in the experimental since the SBT etching process is dominant physical Ar ion bombardments and forms nonvolatile compound. These datum can be used to confirm our previous results of the OES. The plasma density and electron temperature of inductively coupled plasmas were determined by Langmuir probes. The OES results provided a strong support to the etching mechanism in inductively coupled plasma can be used to monitor the chemical and energetic properties of the plasma, providing a basis for control of industrial process.

#### PS-TuP6 CF, CF@sub 2@ and SiF Densities in Inductively Driven Discharges Containing C@sub 2@F@sub 6@, C@sub 4@F@sub 8@ and CHF@sub 3@, G.A. Hebner, Sandia National Laboratories, usa

Laser induced fluorescence was used to measure the spatially resolved CF, CF@sub 2@ and SiF radical density in inductively driven discharges containing fluorocarbon gases. Measurements of the spatially resolved CF density were performed in C@sub 2@F@sub 6@ and CHF@sub 3@

containing discharges as functions of inductive power, pressure and bias condition on a silicon substrate. In addition, CF rotational temperatures were calculated, assuming saturated spectra. Measurements of the spatially resolved CF@sub 2@ and SiF density were performed in C@sub 2@F@sub 6@, C@sub 4@F@sub 8@ and CHF@sub 3@ containing discharges as functions of inductive power, pressure and bias condition. SiF rotational temperatures were also estimated. As the inductive coil power was increased, the SiF density in the center (r = 0 cm) increased while the CF@sub 2@ density decreased and the CF density slightly decreased. In all cases, the radical density in the center of the glow increased with pressure changes from 5 to 30 mTorr while changes in the bias power had little influence on any of the measured radical densities. The spatial distribution of the CF and SiF density peaked in the center of the discharge. The CF@sub 2@ density had a local maximum in the center of the plasma with a decreasing density at the edge of the glow. However, the CF@sub 2@ density outside the glow region was a factor of 2 - 6 higher than the density inside the glow region, depending on the gas. CF and SiF rotational temperatures were between 450 and 750 K. This work was performed at Sandia National Laboratories and supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy.

#### PS-TuP7 Ion Compositions and Energies in Inductively Coupled Discharges Containing SF@sub 6@, A.N. Goyette, Y. Wang, J.K. Olthoff, National Institute of Standards and Technology

High density plasmas generated in mixtures of SF@sub 6@ with rare or simple diatomic gases are involved in many dry etching processes. Plasma etching relies heavily upon surface bombardment by positive ions from the discharge, and experimental determination of the identities and energies of ions striking surfaces exposed to these plasmas contributes to understanding and accurate modeling of these plasmas. We have measured absolute total ion current densities, relative ion intensities, and ion energy distributions (IEDs) at the grounded electrode of an inductivelycoupled Gaseous Electronics Conference (GEC) rf reference cell for discharges generated in pure SF@sub 6@, and in Ar/SF@sub 6@ and O@sub 2@/SF@sub 6@ gas mixtures. Several ions of significant intensity were detected from these plasmas, and the effects of chamber pressure, coil power, and mixture ratio on the fluxes and energies of ions extracted from these discharges were investigated. For pure SF@sub 6@ discharges, SF@sub x@@sup +@ (x = 0-5) ions exhibited the highest fluxes, with S@sup +@ being the dominant ion detected. Mean ion energies were between 15 eV and 20 eV, and were most sensitive to changes in gas mixture ratio. Results of measurements from the mixtures will also be presented.

#### PS-TuP8 Determination and Quantification of the Etch Products of Si with a Chlorine Plasma, G.A. Gaddy, A. Orland, Auburn University; R. Blumenthal. Auburn University. usa

The chlorine plasma etching of silicon has been studied utilizing a novel technique. This technique, supersonic pulse plasma mass spectrometry, allows for the in-situ sampling of the etch plasma at varying heights above the silicon substrate. It has been demonstrated previously that theoretical predictions of the percent dissociation of molecular chlorine in high-density plasmas are only observed using this mass spectral technique. The investigation focuses on the identity and concentrations of the SiCl@sub x@ (x = 1 to 4) products under typical ECR-microwave plasma conditions. Previous studies have shown SiCl to be the primary etch product. The determination of the actual percent yields of all Si etch products may be useful in determining the chemical mechanism for the release of volatile products during the etching of Si.

#### PS-TuP9 Ion Angular Distribution at RF Biased Electrode in Inductively Coupled Plasma, N. Mizutani, K. Yamamuro, T. Hayashi, ULVAC JAPAN, Ltd., Japan

lons play an important role in the plasma etching process. The ions, which were accelerated in the sheath, bombard the substrate with high energies. The etching characteristics, that is to say, the etching rate, the selectivity, the uniformity, and so on, depend on the ion energy. The ion incident angle at the substrate will affect the characteristics in the etching of the fine pattern such as contact holes, because the ion flux at the bottom of the pattern depends on the incident angle. The ion angular distribution (IAD) had been measured at the earthed electrode in the plasma chamber by several groups.@footnote 1@ However, the IAD has never been measured at the RF biased electrode, at which the etching is done. Therefore, we measured the IAD at the RF biased electrode in the inductively coupled

plasma. For the measurement at the RF electrode, the analyzer must be RF floating, that is to say, the electric potential reference of the analyzer must be the potential of the RF electrode.@footnote 2@ Therefore, we have developed such an analyzer. For 2 MHz biased Ar-O@sub 2@ plasma, the IADs were measured by using annular ion collectors that were similar to ones used in Ref. 1. The ion energy distribution (IED) at each ion collector was also measured. For the low gas pressure, 0.4 Pa, the IED was a bimodal distribution at a small incident angle (< 1°), where the vertical incidence corresponds to 0°. The bimodal distribution is due to ions that did not collide in the sheath. The ion flux at the large angle (20°) was very low compared with one at the small angle. For the high pressure, 2.7 Pa, the IED was not the simple bimodal distribution at the small incident angle, and low-energy ions increased relatively. The ion flux at the large angle increased compared with the low-pressure case. The measured behaviors of the IED and IAD can be explained by charge exchange and elastic collisions in the sheath.@footnote 3@ Comparison between the measured IAD and IED and calculated ones will be shown. @FootnoteText@ @footnote 1@ J. R. Woodworth, M. E. Riley, D. C. Meister, B. P. Aragon, M. S. Le and H. H. Sawin, J. Appl. Phys. 80, 1304 (1996). @footnote 2@ N. Mizutani, Y. Nagata, A. Kubo and T. Hayashi, Rev. Sci. Instrum. 69, 1918 (1998). @footnote 3@ N. Mizutani and T. Hayashi, Jpn. J. Appl. Phys. 38, 4206 (1999).

#### PS-TuP10 The Effects of Substrate Temperature on Self-Aligned Contact Etching Process, C.W. Chu, J. Kim, K.-K. Chi, T.-H. Ahn, J.-T. Moon, Samsung Electronics, Korea

In this paper we tried to elucidate the behavior of the selectivity of SiO@sub 2@ to underlying Si@sub 3@N@sub 4@ with the wafer surface temperature. The two kinds of specimen, non-patterned and patterned wafer, were etched in Surface Wave Plasma (Sumitomo) reacto which has an electrostatic chuck. The cooling temperature was varied from -20 to +50 in the C@sub 4@F@sub 8@ plasma. As the wafer temperature goes up, the etch-rates of SiO@sub 2@, Si@sub 3@N@sub 4@ and poly-Si of nonpatterned wafer increased and the selectivity decreased, and vice versa for the patterned specimen. By increasing temperature, the decrease of etchrate of SiO@sub 2@, the increase of selectivity of SiO@sub 2@ to Si@sub 3@N@sub 4@, and the increase of profile angle were observed in the case of the patterned specimen. These observations indicate the important role of the photo-resist erosion and sticking coefficient with a wafer temperature. The effect of carbon enrichment induced by photo-resist erosion was identified by comparing photo-resist-patterned samples with hardmask (poly-Si) patterned ones. The other fact was also supported by the polymer deposition with a low bias power etching in that, the thickness of polymer on the side-wall decreases and the thickness of polymer on the bottom increases as the wafer temperature goes up. In summary, there are two main causes in the effects of substrate temperature, and we can find out the difference between the non-patterned sample etching and the patterned sample etching from the viewpoint of surface reaction.

#### PS-TuP11 Molecular Dynamics Simulation of Oxide Etching by Energetic Halogens, H. Ohta, S. Hamaguchi, Kyoto University, Japan

We have performed molecular dynamics (MD) simulations of silicon dioxide (SiO@sub 2@) etching by energetic halogen (chlorine or fluorine) atoms (or ions) in the energy range of 50-150 eV. To classically simulate such systems, we have constructed Tersoff and Stillinger-Weber type inter-atomic potentials for systems containing Si, O, and Cl (or F) by nonlinearly fitting the inter-atomic potential functions to potential energy data obtained from ab-initio quantum mechanical calculations. Although it is experimentally known that etching rates of oxide by halogen ions are relatively low and it is generally considered that the etching mechanism is essentially physical sputtering, the goal of this study is to clarify details of oxide etching by halogen ions. Our preliminary simulation results based on the newly constructed inter-atomic potentials seem to indicate that, in addition to ordinary physical sputtering, chemical etching is also taking place in oxide etching by halogens. As oxygen atoms with two atomic bonds are more likely to be removed by physical sputtering than silicon atoms with four atomic bonds, oxygen atoms are first removed from the oxide surface by physical sputtering. The remaining excessive silicon atoms are then removed efficiently by the combination of physical and chemical sputtering by halogen ions, as in the case of silicon etching by energetic halogen ions, generating SiCl@sub x@ (SiF@sub x@) compounds as etching products. We have also observed that there are considerable differences in etching mechanisms between chlorine and fluorine ions due to their difference in atomic size. In the meeting, we shall present numerically obtained macroscopic etching properties such as etching rates as well as details of

the microscopic etching mechanism and compare the simulation data with experimental observations.

### PS-TuP12 PIC/MCC Simulation of a 2D Axially Symmetric Dually Frequency RF Plasma Processing System, S. Sunohara, S. Hamaguchi, Kyoto University, Japan

We have developed a Particles-In-Cell / Monte Carlo Collision (PIC/MCC) simulation code for a two-dimensional (2D) axially symmetric radio frequency (RF) driven plasma processing tool. Especially of interest for application of the simulation code is the narrow gap dual frequency reactive ion etching (RIE) system, which is known to achieve well-controlled highly selective SiO@sub 2@ etching with fluorocarbon radicals diluted in Ar discharges. In typical processing conditions for SiO@sub 2@ etching, a gas mixture(mostly Ar, a few % fluorocarbon and oxygen) is introduced to a chamber with the electrode gap of about 2 cm (for 200 mm wafer processing) and the plasma is essentially generated by the primary electrode, which is connected to a higher-frequency, higher-power RF source. The wafer is placed on the secondary cathode and ion bombardment on the wafer is controlled by the RF power applied to the secondary cathode. The narrow gap RIE system has a large surface-area-toplasma-volume(A/V) ratio and the high performance of this system is considered mostly due to the controllability of radical generation at the wall (especially at the primary electrode) by ion bombardment. In our PIC/MCC simulation, we consider only Ar discharges since the discharge conditions are mostly determined by Ar plasmas. Electron impact ionization, excitation, elastic collision of electrons and ions with neutral species, and charge-exchange collisions are all included through the Monte Carlo collision scheme. In low-pressure discharges, we have observed in our simulation bi-Maxwellian electron energy distributions, which implies the collisionless energy transfer to the plasma is dominant. We shall present the dependence of the power deposition, ion bombardmentenergy and plasma uniformity on the gap width, RF frequencies, and RF power.

#### **PS-TuP13 Effect of Time-varying Axial Magnetic Field on Photoresist Ashing in an Inductively Coupled Plasma**, *S.-G. Park*, *H.-Y. Song, B.-H. O*, Inha University, South Korea

Time-varying axial magnetic field coupled with ICP has been found to provide more uniform and higher density plasma with lower electron temperature.@footnote 1@ Weak axial magnetic field can be obtained by a pair of current flowing Helmholtz coils attached to the chamber. This scheme has been applied to etch SiO@sub 2@ and silylated photoresist, where processing pressures are below 50 mTorr and ions are major reaction species. In this work, this method is applied to photoresist ashing, where processing pressure is usually higher than 1 Torr and down stream oxygen radicals are important species. It is found that axial magnetic field improves the ashing rate by 25% and uniformity of 4% over 8" wafer, and that the optimun frequency of the magnetic field is 60Hz. Optical emission spectroscopy is used to characterize the effect of the magnetic field. Effect of aluminum baffle inserted between plasma and wafers is also investigated in this system. @FootnoteText@ @footnote 1@ Beom-hoan O, Jae-seong Jeong, Se-Geun Park, "Improvement of ICP plasma with periodic control of axial magnetic field", Surface and Coatings Technology, 120-121(1999) 752-756.

#### **PS-TuP14** The Characteristics of Atmospheric Pressure Glow Discharge formed by Capillary Electrode, *Y.H. Lee*, *C.H. Jeong*, *G.Y. Yeom*, Sungkyunkwan University, Korea

In industrial plasma processes, vacuum systems have been generally used for thin film deposition, dry etching, and surface treatments. To remove costly vacuum systems and to apply to various other situations, low temperature plasmas generated at atmospheric pressure such as dielectric barrier discharges, atmospheric microwave discharges, etc. are actively studied in these days. In this study, the characteristics of low temperature atmospheric plasmas generated using capillary electrodes were investigated. The characteristics of the plasmas were studied as a function of capillary aspect ratios, input power, frequency of input power, electrode distance, and gas mixtures and their flow rate, using a high voltage probe(Tektrionix P6015) and current probe(Pearsonelectronics 6600). Reactive gases such as He/ O@sub 2@ were also used and their ionization and dissociation properties were investigated using a mass spectrometer and optical emission spectroscopy (OES). The voltage between electrodes measured by high voltage probe increased with the increase of input power, the increase of electrode distance, the decrease of He flow rate, and the increase of O@sub 2@ flow rate. The increase of capillary aspect ratio also increased the discharge voltage, however, more stable capillary discharge was obtained by the increased current limiting of the high aspect

ratio capillary. Increased ionization and dissociation of the plasma species could be observed by OES with the increase of input power in a He/ O@sub 2@ mixture. However, with the increase of O@sub 2@ flow rate in a constant He flow rate, the emission peaks from He decreased due to the increased electron consumption by oxygen while the emission peaks from O@sub 2@ @super -@ and O increased due to the increased ionization and dissociation rates with the increase of oxygen concentration in the He/O@sub 2@ gas mixture. Using He/O@sub 2@ gas mixtures, organic materials such as photoresist could be successfully removed.

**PS-TuP15** Spatial Distribution of Carbon Species in Laser Ablation of Graphite Target, *T. Ikegami, S. Ishibashi, Y. Yamagata, K. Ebihara,* Kumamoto University, Japan; *R.K. Thareja,* Indian Institute of Technology Kanpur, India; *J. Narayan,* North Carolina State University

A DLC film has excellent properties like a diamond and its applications are expected in many fields. Pulsed laser deposition (PLD) is one of methods that can deposit hydrogen free DLC films. In order to optimize the process it is necessary to understand the ablation process. Many form of carbon species exist in the plume, therefore, their number densities and energy states seem to affect the characteristic of the deposited DLC films. However, it has not been well understood about relation between their behavior and the film properties. Emission spectroscopic analysis is usually used to the plasma plume measurement, but this method give no information on non-emissive. A carbon plasma plume produced by the KrF excimer laser ablation of a graphite target was measured by the laser induced fluorescence (LIF) method. C@sub 2@ molecules produced from the target were excited by a probe laser using C@sub 2@ swan band a@super 3@@PI@@sub u@-d@super 3@@PI@@sub g@. Two-d imensional LIF signals from C@sub 2@ molecules were measured using an ICCD camera at several delay time of the probe laser incidence from the KrF laser irradiation. Experimental results showed that C@sub 2@ molecules have relatively low internal and kinetic energy and locally exist near the target and its density decreased with increasing laser fluence.

#### **PS-TuP16** Controlled Plasma Characteristics by a Novel Method of Enhanced Inductively Coupled Plasma, S.-H. Rha, C.-W. Kim, S.-G. Park, B.-H. O, Inha University, South Korea

It is important to control the electron energy distribution to have high quality plasma process. A conventional inductively coupled plasma(ICP) source with 13.56MHz power is not adequate for low damage sub-half micron patterning process due to higher electron temperature. Only the pulsed plasma technique seems to provide low electron temperature, and thus low process damage. Recently, a novel method proposed by us, named as 'Enhanced-ICP', which uses periodic weak axial magnetic field added to a normal ICP source, has shown great improvement in etch characteristics. Novel changes of plasma characteristics according to the frequency of time-varying axial magnetic field have been observed by a time-resolved analysis of Langmuir probe. It is found that the plasma density is increased while the electron temperature is lowered in E-ICP. Furthermore, the spatial plasma distribution is also homogenized by this method. Many evidences on improvement of electron energy distribution and spatial plasma distribution will be discussed for various cases using time-resolved analysis of Langmuir probe and optical emission spectroscopy. Theoretical analysis for this phenom is presented in this paper.

#### **PS-TuP17 Radio Frequency Biasing of an Ion-Ion Plasma**, *B. Ramamurthi*, University of Houston; *V. Midha*, General Electric; *D.J. Economou*, University of Houston

A one-dimensional fluid model for simulating the effects of RF bias applied to an ion-ion plasma was developed. The full ion momentum and continuity equations were coupled to the Poisson equation for the electrostatic field. Special emphasis was placed on the effect of applied bias frequency. Due to the lower temperature and greater mass of negative-ions compared to electrons, the sheath structure in ion-ion plasmas changes significantly as the bias frequency is varied. For low bias frequencies (100 kHz), the charge distribution in the sheath is monotonic (switching from positive to negative) during each half cycle. For intermediate frequencies ( 10 MHz), when the bias period approaches the ion transit time through the sheath, double layers form with both positive and negative charges coexisting in the sheath. For high frequencies, beyond the plasma frequency (60 MHz), plasma waves are launched from the bulk plasma and the sheath consists of multiple peaks of positive and negative charge (multiple double layers). For a relatively large range of bias frequencies (up to the plasma frequency), each electrode is bombarded alternately by high energy positive and negative ions during an RF bias

cycle. For bias frequencies greater than the plasma frequency, however, the electrode is bombarded simultaneously by low energy positive and negative ions with ion energies approaching the ion temperature. It was also found that the ion energy increases with the applied bias potential. At relatively high pressures (greater than 20 mTorr), the ion energy at low frequencies (100 kHz) is limited by collisions and the peak ion energy may be increased by using a higher bias frequency (10 MHz). At lower pressures, however, the effect of collisions is mitigated while the effect of ion transit time becomes significant as the bias frequency increases. In this case, a low bias frequency is favorable for extracting high energy ions from the plasma.

#### PS-TuP18 Comparative Study of W, WN@sub x@ and Si RIE in SF@sub 6@/Ar using Actinometry Technique, S.A. Moshkalyov, C. Reyes-Betanzo, UNICAMP, Brazil; A.C. Ramos, UNICAMP-IFGW, Brazil; A. Diniz, J.W. Swart, UNICAMP, Brazil

The use of tungsten thin films in micro-fabrication attracts much attention. For etching of W and WN@sub x@ films, SF@sub 6@ is commonly used which provides high etch rates. However, for RIE reactors considerable undercutting of W/WN@sub x@ in SF@sub 6@ was usually reported. The objective of this study was to find conditions of anisotropic etching of tungsten films using conventional RIE medium-pressure reactor. To characterize the density of fluorine radicals in the plasma, an optical emission spectroscopy (actinometry) was employed. To provide considerable variation of radical/ion fluxes to the processed surfaces, the SF@sub 6@/Ar ratio was varied widely. Two sets of experiments were performed keeping either RF power or DC bias constant while changing the SE@sub 6@/Ar ratio. The results show that the silicon etch rate is nearly proportional to the fluorine radical density with only the minor effect of the DC bias (ion energy). Thus in the Si-F system the chemical (spontaneous) etching is the dominant mechanism. In contrast, in tungsten etching, the role of ion-induced effects is much more pronounced. Furthemore, the tungsten etch rate dependence on a fluorine density has a threshold behavior with the threshold depending on the ion energy. This indicates that at a relatively small (not saturated) surface coverage by fluorine, the ion bombardment provides strong enhancement of surface processes leading to efficient formation and desorption of volatile WF@sub 6@ etch products (most likely, an ion-induced associative desorption). Under these conditions, highly anisotropic etching of tungsten and tungsten nitride have been achieved using a conventional RIE reactor at relatively high etch rates (>100 nm/min).

#### PS-TuP19 Improved Etch Characteristics of SiO@sub2@ by the Enhanced Inductively Coupled Plasma, S.-B. Cho, H.-Y. Song, S.-G. Park, B.-H. O, Inha University, South Korea

It has been known that generation of active species and passivation layers is very important for etching contact holes of high aspect ration in sub-half micron technolgy. Some of the solutions are to use high C/F ratio chemistry and/or to apply pulsed plasma technique. In this work, we suggest better and simpler method, which was time-varying axial magnetic field applied to a normal ICP source. Enhanced ICP has a pair of external coils attached to the conventional ICP, and periodic weak axial magnetic field can be obtained by changing the magnitude and direction of the current through the coils periodically. Etch rate, uniformity and micro-loading effect can be greatly improved by changing the frequency. The etched characteristics by CF@sub4@ and C@sub4@F@sub8@ plasma in E-ICP is very interesting in that the bonding energy of C-C and C-F are different and the electron distribution can be controlled in E-ICP. The SEM pictures show effective removal of micro-loading effect and micro-trench problem, for an optimized E-ICP. More details on E-ICP operation for SiO@sub2@ etch and the mixture effects of additional gas (oxygen and hydrogen) are discussed further.

#### PS-TuP20 Silicon Surface Roughness Induced by Reactive Ion Etching in SF@sub 6@ and SF@sub 6@/O@sub 2@ Plasmas, S.A. Moshkalyov, UNICAMP-University of Campinas, Brazil; P. Verdonck, R.D. Mansano, University of São Paulo - USP, Brazil; M. Cotta, UNICAMP, Brazil

With the trend of continuous minimization of device structures in microfabrication, surface roughness induced by plasma processing becomes an important issue. The problem is of particular importance in the case of deep trench etching of silicon for MEMS applications. Mechanisms of roughness formation and development during plasma processing are not well understood. Surface roughness is closely related to the energies and flux densities of ions and reactive radicals coming from the plasma to the processed surface. A study of the evolution of surface morphology can provide better understanding of etching mechanisms. New opportunities for this kind of study arose with the recent introduction of high-resolution local probes like AFM, which allow to obtain real spatial surface images. Experiments were performed in a RF-driven RIE plasma etcher with SF@sub 6@ and SF@sub 6@/O@sub 2@ gas mixtures at medium gas pressures (50-150 mTorr). Small (100) silicon samples with an AI mask were etched with etch time varying from 2 to 30 min. After the process, etch rates were measured and surface morphology was analyzed by AFM in frames ranging from 2x2 mkm to 40x40 mkm. The results show a significant difference in roughness evolution for SF@sub 6@ and SF@sub 6@/O@sub 2@. For both cases, the roughness parameter rises almost linearly with time, but its rise is faster for oxygen contaning mixtures. For short etching times (2 min.) and small/medium oxygen content (10-30%) the rms roughness parameter was even slightly smaller for gas mixture (21-24 nm) than for pure SF@sub 6@ (26 nm). Furthemore, in the former case the surface morhology is distinctly more regular. The mechanisms reponsible for the formation of surface roughness in both cases are discussed.

#### PS-TuP21 Transmission Line Effects and Chlorine Plasma Characterization in an Inductively Coupled Plasma Etch Reactor, *M.H. Khater*, *L.J. Overzet*, University of Texas at Dallas

Transmission line (i.e. standing wave) effects in inductively coupled plasma sources impact the plasma and processing uniformity. In this work we show standing wave effects on the symmetry and uniformity of power deposition, plasma parameters, and polysilicon etch in chlorine plasma. A new ICP source design, which allows better control of field profiles azimuthal symmetry, is compared to a standard spiral planar coil on an industrial plasma etch reactor. B-dot probe measurements of the free space electromagnetic fields in (r,@theta@) plane for both sources showed improved azimuthal symmetry for the new source. The planar coil generated an azimuthal electric field, E@sub theta@, with a local maxima near the grounded (i.e. high current) lead and a significant azimuthal variations. A three-dimensional electromagnetic field model that includes standing wave effects was developed for both sources. The sources were modeled as uniform transmission lines and the current variation along their lengths was estimated from standard transmission line theory. The model showed good agreement with the measured field profiles. Langmuir probe measurements of chlorine plasma parameters spatial profiles near the dielectric window also showed improved azimuthal symmetry of power deposition with the new source. Parametric characterization of chlorine plasma parameters and their spatial profiles generated with the new source will also be shown. Plasma parameters and their spatial profiles exhibited different scaling behaviors with power and pressure in the power deposition region and the wafer plane. Polysilicon etch rate profiles on 150 mm wafers showed improved azimuthal symmetry and uniformity with the new source.

#### PS-TuP22 Penetration of Electromagnetic Fields in ICP, Weakly Magnetized ICP, and Low-B Helicon Discharges, J.D. Evans, F.F. Chen, D. Arnush, University of California, Los Angeles

Due to renewed interest by the plasma processing community, the physics of the penetration of electric and magnetic fields in low pressure, weakly ionized plasmas is an area of active research. Penetration of induced Bfields in ICP, weakly magnetized ICP, and low-field helicon discharges is investigated in a device consisting of a dome-shaped Pyrex top attached to a magnetic bucket. The antenna consists of a multi-turn loop of wire wrapped around the top (radius = R@sub top@), and B@sub o@ is produced by a magnet coil located near the antenna. B@sub z@-dot probes are used to measure B@sub z@-field profiles. B@sub z@ decays approximately exponentially with decreasing R in most cases. Characteristic decay lengths of B@sub z@ (L@sub sd@) are measured as P@sub o@ is varied. Good agreement between experiment and collisional skin depth theory is observed for f@sub RF@ = 2MHz when non-uniform density profiles are taken into account. Experimental values greatly exceed collisional theoretical predictions for f@sub RF@=6.78MHz, in qualitative agreement with anomalous skin effect (ASE) theory. Variations of L@sub sd@ with B@sub o@ have also been measured, and good agreement between experiment and collisional theory is observed in most cases. Regions of enhanced B@sub z@ ("wings") are observed near the edge for B@sub o@>0, in qualitative agreement with code predictions when axial boundary conditions are accounted for. As B@sub o@ increases, L@sub sd@ increases, and B@sub z@ in the interior increases. Coupling to a low-B@sub o@ helicon mode is expected when L@sub sd@ @>=@ R@sub top@. Under these conditions, the B@sub z@-field amplitude behavior changes from evanescence to propagation. At higher powers and neutral pressures, large phase shifts in B@sub z@, apparent "nodes" in B@sub z@ amplitude profiles, and other interference-type phenomena are observed, even in highly collisional regimes where ASE is not predicted to occur.

**PS-TuP23** Ion-Iion Plasma Formation in Chlorine in an Inductively Coupled Plasma Etch Reactor, *M.H. Khater, S.K. Kanakasabapathy, L.J. Overzet,* University of Texas at Dallas

We will show time-resolved characteristics of pulsed chlorine plasmas in an industrial, inductively coupled plasma etch reactor. Using pulsed-plasmas may enhance processing and reduce charge-up damage of sub-micron features. Electron free or "ion-ion" plasma forms during the afterglow of highly electronegative discharges (e.g. Cl@sub 2@) due to electron attachment. The electron loss can be characterized by a "transition time" after which ion-ion plasma exists within the reactor. Such electron free plasma can provide both positive and negative ion fluxes to a substrate potentially reducing charge-up damage as well as enabling negative ion assisted processing. The transition time to ion-ion plasma (8-25 µsec) is mostly dependent on pressure and power while varying only slightly with pulse frequency and duty ratio. Larger Cl@sub 2@ concentrations at high pressure and/or lower power discharges result in smaller transition times due to dissociative attachment. Measurements of the plasma parameters time evolution were obtained at 1 cm above the substrate for 500 W peak power, 1 kHz pulse frequency and 50% duty ratio. The ion densities generally decreased as expected during the afterglow, except they increased slightly near the end of the afterglow at higher pressures. This suggests a transport of jons from the source towards the substrate. Spatiotemporal measurements showed electron and ion density profiles that peaked at the center during the active glow with similar uniformities to those obtained in CW operation. The ion density uniformity improved gradually during the beginning of the afterglow (~ factor of 2) but degraded back to active glow values near the end of the afterglow. This is likely related to the ion loss mechanisms. Ion-ion recombination should tend to flatten the ion density profile in the early afterglow whereas ion loss due to diffusion should tend to cause a peak in the center and dominate at the end of the afterglow.

# PS-TuP24 Effect of Temperature (or Heat) on the Etch Rate of Iridium and Platinum in CF@sub 4@/O@sub 2@ Plasma, H. Ying, J.S. Maa, F. Zhang, S.T. Hsu, Sharp Laboratories of America, Inc.

Iridium and platinum films are often used as electrode materials in ferroelectric devices. In this work, we demonstrated that the substrate temperature plays an important role in the etching of iridium and platinum when etched in a CF@sub 4@/O@sub 2@ plasma. The etching was performed in an Electron Cyclotron Resonance (ECR) plasma reactor. The wafer was placed on a heated chuck during etching. Wafer temperature was maintained in the range of 70°C to 250°C before etching. An RF power was applied to the wafer chuck to generate a self-bias potential. At temperatures below 100°C, the iridium etch rate was low (~200 Å/min). The etch rate increased with the increase of temperature, and reached ~1500 Å/min at above 200°C. Platinum showed a low etch rate below 150°C, then also increased to ~1500 Å/min at higher temperature. In both cases, there is a transition from low etch rate to high etch rate. The transition occurred at a slightly higher temperature for the case of platinum etching. The increase of etch rate at higher temperature was believed due to the formation of volatile compound of IrF@sub 6@ and PtF@sub 6@.

#### PS-TuP25 Process Performance Evaluation of Low Damage Sources, X. Tang, D. Manos, College of William and Mary

We have performed a comparative study to characterize and evaluate the performance of two low damage sources, a surface reflection neutral source and a pulsed ICP source. The neutral stream was characterized using sensitive momentum and microcalorimetric energy analyzers to detemine that the neutral energy of our source is tunable between 3-6 eV and that the neutral flux is on the order of 3 x 10@super 15@cm@super -2@ s@super -1@. These results are in excellent agreement with earlier published flux values@footnote 1@ inferred from the stripping rate measurements and are also in excellent agreement with our previous Monte Carlo simulations.@footnote 2@ A pulsed rfi plasma source (200Hz to 10kHz) was also characterized using a Langmuir probes deploying two different data analysis methods to extract plasma density and electron temperature and to follow mode transitions in the source operation. The probe measurements indicate that there is an optimal pulse frequency in our source at around 1kHz. We have performed a zero-dimensional, explicit-time, kinetic model simulation of the pulsed behavior of this source which agrees very well with the observed values of the density, temperature, and trends of pressure and power dependence and with the temporal behavior as a function of pulse length and duty cycle. Experimental studies comparing the neutral stream to direct and downstream plasma exposure indicates that fast neutrals induces much

lesss damage than exposure to the pulsed plasma source and that most of the damage from neutral operation comes from exposure to UV photons. Preliminary experiments using the fast neutral bombardment to do low-temperature growth of both stable and metastable films in a charge-free environment will also be presented in this paper. @FootnoteText@ @footnote 1@X.Tang, C.A.Nichols, and D.M.Manos, J. Appl. Phys. 86:2419, 1999 @footnote 2@C.Nichols and D.Manos, J. Appl.Phys. 80:2643,1996.

### PS-TuP26 The Effects of Electrostatic Bias on the Radial Plasma Potential Profile in a Helicon Plasma, *S.W. Lee*, *S.H. Jun*, *S.H. Uhm*, *Y. Lee*, *H.Y. Chang*, Korea Advanced Institute of Science and Technology, Republic of Korea

The effects of electrostatic bias on the radial plasma potential profile has been studied in a helicon plasma. Two types of electrode - ring and planar type - were used. Electrodes were floated, negatively, and positively biased. The radial profile of ion density and plasma potential were measured with Langmuir probe. The ion velocity distribution function was measured with Doppler shifted laser induced fluorescence technique. The floating and negatively biased electrode gives similar result on plasma potential and ion density. The positive bias increases the plasma potential as high as the electrode voltage. The hollow plasma potential profile was formed when ring electrode was used. The profile is affected by gas pressure, ion density profile, static magnetic field, electron temperature, ion temperature, and ion flux. We could explain the phenomena with the results of LIF and Langmuir probe measurement.

# **PS-TuP27** New Large Area Plasma Source, Y. Lee, D.S. Lee, S.W. Lee, H.Y. Chang, Korea Advanced Institute of Science and Technology, Republic of Korea

A new large area plasma source for 300mm wafer processing were developed and studied. The antenna system of the source consists of 3-turn circular coils connected parallely and the outer coil connected with series to an additional capacitor which is able to controll the antenna current distribution. It was found that the source have several advantages compared to other popular plasma sources. Firstly, the current distribution of the antenna by changing capacitance of the capacitor can be controlled so that the good spatial uniforminty of electron density is obtained. Secondly, the source has very low antenna voltage because the antenna has very low impedance near LC resonance point. At 3 - 30 MHz and 2 - 20 mTorr of argon, electron density uniformity within 3% was achieved.

#### PS-TuP28 Antenna Configurations for Large Area rf Inductive Plasma Sources, *M.M. Patterson*, University of Wisconsin, Madison, US; *T. Lho*, *A.E. Wendt*, *N. Hershkowitz*, University of Wisconsin, Madison

Industrial demands for uniform, high density, low pressure plasma processing over large areas (roughly 300 cm diameter circular substrates) motivate the study of alternatives to the standard spiral antenna design for inductive plasmas. Scaling of the spiral design suffers from several complications including increased voltage requirements (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. A possible solution to these problems is to change the connection between the concentric circular antenna loops from serial (spiral) to parallel. This lowers the net inductance (decreasing voltage requirements) and allows for control over the current in concentric loops by connecting an appropriate lumped inductor between them, enhancing uniformity. We have constructed several circular loops, 10, 20, 30, and 40 cm in diameter for use in a planar inductive plasma source of 64 cm inner diameter. Several types of connections are possible: two loops can be connected either in series or parallel, loops can be driven singularly, and more than two loops can be connected and driven in some combination of serial and parallel connections. Langmuir probe measurements of radial ion saturation current profiles in argon discharges show that good uniformity can be achieved over 30 cm diameter circular areas by choosing the appropriate inductor. Preliminary results also indicate that the ratio of inner and outer loop diameters significantly affects uniformity. We will present results that compare the spatial electron density profile with parallel versus serial connection, loop diameter, and the ratio of inner and outer loop diameters, for both serial and parallel connections.

**PS-TuP29** Dry Etching of SrBi2Ta2O9 Thin Films in Cl2/NF3/O2/Ar Inductively Coupled Plasmas, Y.-H. Im, R.-J. Choi, Chonbuk National University, Korea; Y.B. Hahn, Chonbuk National University, Korea, South Korea; J.K. Lee, Korea Institute of Science and Technology

Inductively coupled plasma etching of SrBi2Ta2O9 (SBT) films for FRAM applications has been carried out in Cl2/NF3/O2/Ar discharges. The etch characteristics and ferroelectric properties of SBT films prepared by magnetron sputtering were investigated in terms of etch rate and P-E hysteresis curve. The etch rates were dependent on plasma parameters such as ICP source power, rf chcuk power and etch gas combinations. Ar plasma showed fastest etch rate, but resulted in severe damage to ferroelectric layers. Addition of oxygen to the etch gas combination reduced etch damage. The electrical properties of the SBT films were quite dependent on etch conditions. The decreased remanent polarization of etched Pt/SBT/Pt structure was rectified after annealing in oxygen atmosphere.

### PS-TuP30 Ionized Magnetron Sputter Deposition of MgO for Protective Layers in PDP, J. Joo, Kunsan National University, Korea

MgO is known to be a good candidate for protective materials in Plasma Display Panel industries. Electron beam evaporation has been used to deposit MgO on glass substrates, but it has some problems in large scale production equipment for panels larger than 55 inch in diagonal. Currently, in-line type magnetron sputtering machine appears to be a solution in thickness uniformity point of view. HCD based ion plating was tried and produced very dense layer of MgO along with longer service life as a protective layer. In this study, reactive ionized PVD is tried in depositing MgO using 2 MHz ICP source along with bipolar pulsed dc sputtering power source for Mg metal target. Characteristics of deposited MgO was analysed by XRD, AFM, transparency and erosion rate. As an in- situ analysis, optical emission spectroscopy was used to monitor dissociation level of oxygen and ionization level of sputtered Mg. In mass flow rate of Ar:O2 = 10 : 2, transparent, hard MgO films were obtained lower than 300C of substrate temperature. Also the post treatment using in-situ oxygen ICP was tried to stabilized the as-deposited surface of MgO. Crystal preferred orientation varied from (111), (200) to (220) and by optimizing the plasma condition, films having similar crystalinity of bulk (JCPDS data) was successfully obtained.

# PS-TuP31 Plasma Characterization and Film Structure Control for ZrO2/Y2O3 Laser Ablation in Different Environments, A.A. Voevodin, J.G. Jones, J.S. Zabinski, Air Force Research Laboratory, WPAFB

Laser ablation deposition of highly oriented yttria stabilized zirconia (YSZ) films is important for various technological applications and depends critically on the selection of background environment, with low pressure oxygen being the most common choice. Here, the spatial-temporal distribution of YSZ ablation plasma chemistry, excitation states, and energy was determined for ablations in vacuum, low pressure O2, and low pressure Ar. For this purpose, fluorescence spectroscopy, element specific imaging techniques, and time-of-flight experiments were used. It was found that an Ar background considerably promotes excitation and ionization of zirconium during the first 1-3 ï-s after the laser strike. There is much less zirconium excitation in an O2 background, where a large fraction of atomic oxygen with a broad spatial distribution was found. ZrO and YO molecules were observed in both environments. Kinetic energies of neutral species were reduced by about a factor of two in Ar and O2 backgrounds compared to vacuum. This was not observed for Zr1+ species, which maintained about 100-120 eV mean kinetic energy nearly independently of the background. The results of the plasma analyses were used for the film composition and structure control. In particular, films with [001] orientation, with respect to the substrate surface, were produced at near room temperature on various single crystal and polycrystalline substrates. Correlation between deposition parameters, plasma characteristics, and film properties are discussed.

## Wednesday Morning, October 4, 2000

### Incorporating Principles of Industrial Ecology Room 304 - Session IE+PS+MS+SE-WeM

#### Environmentally Friendly Process Development Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am IE+PS+MS+SE-WeM1 CVD Films as Directly Patternable Low-k Dielectrics, K.K. Gleason, H.G. Pryce Lewis, Massachusetts Institute of Technology; G.L. Weibel, C.K. Ober, Cornell University INVITED As microelectronic feature sizes decrease to 100-nm and below, major advances in both interconnect and lithographic technologies are necessary. Novel low-k candidates being assessed include fluorine- and siliconcontaining materials produced by chemical vapor deposition (CVD). Fluorine- and silicon-containing polymeric materials are also ideal resist candidates for 157-nm photolithography, as conventional photoresists are opaque at this wavelength. In this paper, we present a collaboration aimed at merging the role of sacrificial resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a low-k fluorocarbon or organosilicon material is deposited by CVD, exposed, and developed using no wet processing. In our scheme, a film is deposited using hot-filament CVD, a non-plasma technique which offers the ability to tailor film chemistries. The film is masked and exposed using e-beam or a 157-nm source, and developed using supercritical CO@sub 2@ as a dry developing medium. The patterned film then serves as a low-k material compatible with metallization schemes such as the damascene process. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. The CVD process and the use of dry development also offer environmental, safety and health advantages over solvent-based spin-on coating and aqueous development. Positivetone contrast has been demonstrated in fluorocarbon CVD films and fullydeveloped images of 0.25-micron have been demonstrated from e-beam exposure. We are presently working to enhance sensitivity and optimize image resolution.

#### 9:00am IE+PS+MS+SE-WeM3 Characterization of Remote Plasma Clean Process for Plasma CVD Chamber, *T. Tanaka*, *T. Nowak*, *M. Seamons*, *B.H. Kim, K. Lai, M. Cox, P. Loewenhardt, D. Silvetti, S. Shamouilian*, Applied Materials Inc.

Remote plasma cleaning of CVD process chambers has proven to be more efficient than conventional in-situ plasma cleaning in terms of higher throughput and higher gas breakdown efficiency. It is still important, however, to maximize the efficiency of the remote plasma clean process because of the potential environmental impact and the cost of process gases. The remote clean process involves three steps: generation of reactive species (mostly fluorine atoms) in a remote plasma source, transport of the reactive gas, and the cleaning reaction in the CVD chamber. We studied the efficiency of the process in each step. Since accurate direct measurement of the atomic fluorine concentration in the various parts of the CVD reactor is difficult, we used etching of thermal oxide wafer coupons to estimate the relative distribution of atomic fluorine within the reactor. Source dissociation efficiency was studied using an indirect technique based on correlation of pressure to effluent composition. We found that it requires approximately 24eV to break down each NF@sub 3@ molecule. This translates to 1.7W/sccm of NF@sub 3@ flow. This was seen to be approximately the same for both a microwave discharge operating at 2.45GHz and an inductively coupled plasma at 13.56MHz. Results characterizing the transport step demonstrate the importance of system design on minimizing recombination losses of the reactive species which, for a parallel plate reactor, can be as high as 50% of the atomic fluorine generated in the remote plasma source. The experimental results are compared with a simple model, which describes the general behavior of the cleaning process.

#### 9:20am IE+PS+MS+SE-WeM4 Silicon Oxide Contact Hole Etching Process Employing Environmentally Harmonized Technique, K. Fujita, M. Hori, T. Goto, Nagoya University, Japan; M. Ito, Wakayama University, Japan

Etching process of SiO@sub 2@ contact holes in ULSI has been developed by using high-density plasmas employing stable PFC gases. PFC gases, however, cause a serious environmental problem, namely global warming and hereby the uses of fluorocarbon gases would be restricted in the near future. Recently, we proposed environmentally harmonized technique replacing stable PFC gases for preventing global warming, where polytetrafluoroethylene (PTFE) is evaporated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) are injected into ECR plasma reactor from externally. This technique, therefore, enables us to achieve a novel plasma process with new gas chemistries. In this study, this system has been successfully applied to ECR plasma etching of SiO@sub 2@ contact hole and the behavior of CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). The high SiO@sub 2@ etching rate of 780 nm/min was obtained at a microwave power of 400 W, a pressure of 2.7 Pa, a total flow rate of 80 sccm and a bias voltage of -450 V. Dependence of contact hole etching characteristics on Ar dilution and pressure has been investigated. Anisotropy of contact hole etching was improved with increasing the Ar dilution ratio and decreasing the pressure because the fluorocarbon polymer deposition was suppressed at the higher Ar dilution and the lower pressure. IRLAS measurements indicate CF@sub 2@ radicals and higher radicals (C@sub x@F@sub y@) have the good relation with the polymer deposition. The anisotropic contact hole etching was achieved at an Ar dilution ratio of 90 %, a pressure of 0.4 Pa and the etching rate of SiO@sub 2@, selectivity of SiO@sub 2@ to Si and selectivity of SiO@sub 2@ to resist were 340 nm/min, 31 and 6.4, respectively. These results indicate that this environmentally harmonized technique will propose the alternative etching system replacing PFC gases.

# 9:40am IE+PS+MS+SE-WeM5 Photocatalytic, Anti-fogging Mirror, K. Takagi, ULVAC Japan, Ltd., Japan; H. Hiraiwa, T. Makimoto, T. Negishi, ULVAC Japan, Ltd.

Recently, environmental pollution is growing more serious everyday, and it is urgently required to develop resource-saving and non-chemical products, which may save and even purify the nature. In such circumstances, titanium dioxide (TiO@sub 2@) thin coating film has come into the spotlight as a savior of the environmental problems. Because of its attractive photocatalytic natures, such as anti-bacterial, self-cleaning, decomposition of organic substances, and super-hydrophilic natures, TiO@sub 2@ has been studied and developed energetically in these days. Already, its super-hydrophilic and self-cleaning natures are applied to automobiles' anti-fogging side mirrors, which are now in practical use, and ULVAC Japan is one of the top makers for manufacturing vacuum deposition system for anti-fogging mirrors. The film architecture of this mirror is the double layer of SiO@sub 2@ / TiO@sub 2@ on the substrate coated by E/B evaporation or sputtering. The photocatalytic natures are as follows; 1. The contact angle of water on this surface is less than 10@Ao@ after irradiation of Blacklight, on which the engine oil is spreaded and cleaned by washing. 2. The contact angle keeps less than 10@Ao@ when this sample is preserved in the dark room. This report describes current developmental status of vacuum deposition system for TiO@sub 2@/SiO@sub 2@ thin film coating that is applied to automobile-mounted photocatalytic mirrors and is useful for environment saving and purification.

#### 10:00am IE+PS+MS+SE-WeM6 Low-k Materials Etching in Magnetic Neutral Loop Discharge Plasma, Y. Morikawa, S. Yasunami, ULVAC JAPAN Ltd.; W. Chen, T. Hayashi, ULVAC JAPAN Ltd., Japan; H. Yamakawa, T. Uchida, ULVAC JAPAN Ltd.

Many low-k materials, like Si containing inorganic / organic compounds, purely organic compounds and porous silicate glass, are proposed and examined as the interlayer dielectric one. The magnetic neutral loop discharge ( NLD ) plasma is very useful for very fine pattern etching process, because the NLD plasma has high density and low temperature characteristics and tends to form uniform density distribution on the substrate, at lower pressure region than 1 Pa under 13.56 MHz oscillating induction field.@footnote 1-3@ So we adopted the NLD plasma to etch organic low-k materials, with very high etch rate over 900 nm/min by using NH@sub 3@. An etching issue for the purely organic low-k materials is bowing in the hole smaller than 200nm in diameter, probably caused by reaction of the hole-wall surface with hydrogen atoms. Based on this consideration, we carried out the etching by using nitrogen gas mixed with a low concentration of hydrogen gas in low pressures below 1 Pa. The etch rate increased abruptly at hydrogen addition of a few quantity and approached gradually to a constant value at 20%. But the bowing size became larger above hydrogen mixed ratio of 20%. So we measured mass spectra of ion species produced in the plasma to know the mechanism. It was found that intensity of N2H+ also increased abruptly and then was close to a constant value at 20%. The other species did not show similar tendency. It is deduced from this result that N2H+ ion may participate in main etching reaction to obtain the conformal etched profile. Etching characteristics for OSG, pure organic low-k materials and porous silicate glass will be shown. @FootnoteText@@footnote 1@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : Jpn. J. Appl. Phys.,

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38 (1999) 4296 @footnote 2@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita and T.Uchida : Vacuum, 53 (1999) 29 @footnote 3@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : J. Vac. Sci. Technol. A17(5), (1999) 2546.

### Plasma Science and Technology Room 311 - Session PS+MS-WeM

### **Plasma-Induced Damage**

Moderator: L.J. Overzet, University of Texas, Dallas

8:20am **PS+MS-WeM1 Plasma-Induced Charging Gate Oxide Pinhole Formation**, **T.C. Ang**, *S.Y. Loong*, *P.I. Ong*, *W.B. Loh*, Chartered Semiconductor Manufacturing, Singapore; *Y.W. Teh*, Nanyang Technological University, Singapore

Plasma process induced charging damage to gate oxide is a growing concern in ULSI MOS device fabrication. This is due to gate oxide thinning resulting from continuous CMOS downsizing and increasing use of high density plasma (HDP) tools. In this paper, we study the extent of the plasma induced damage resulting from HDP inter-metal dielectric deposition process in 0.18um transistor technology. Gate oxide pinhole formation resulting from plasma induced charging damage was observed above a threshold ion density. Transistor test structures with different types of antennas and antenna ratios were used to monitor the plasma damage. The extent of the plasma charging damage was evaluated through shift in gate leakage, threshold voltage and transconductance from a reference transistor with no antenna attached. Each of these parameters were measured for a large number of transistors in order to statistically assess the level of plasma based gate oxide damage. Gate oxide pinhole formation was observed in transistors with antenna ratios above a certain value. The pinholes were caused by localized breakthrough of the gate oxide resulting from charge imbalance in the plasma and are only present when the charge imbalance exceeds a threshold value. Based on our results, we have determined the threshold value for charge imbalance and ion density to cause gate oxide pinhole formation. We have also developed a novel integration scheme which is effective in reducing the charging damage from the high density plasma process significantly and no gate oxide pinholes were observed with the implementation of this scheme.

8:40am PS+MS-WeM2 Effects of Plasma-induced Charging Damages on Thin Gate Oxide during Plasma Etching Processes, Y.-K. Kim, K.-O. Klm, J.-V. Kim, C. J. Chai, J.W. Kim, Humdai Floatenia Induction Co., Itad. Konst.

Y. Kim, C.J. Choi, J.W. Kim, Hyundai Electronics Industries Co., Ltd., Korea Using the plasma damage monitoring (PDM) system, we investigated the plasma-induced charging damage in the thermally-grown SiO@sub 2@ on p-type Si substrates after plasma etching of gate electrode. Recently, the technique has been frequently employed to monitor oxide damages induced by plasma processes. It determines the changes in oxide electrical properties such as flatband voltage (V@sub fb@), oxide resistivity (@rho@@sub ox@), effective charges (Q@sub eff@), interface trap density (D@sub it@), etc. The measured Q@sub eff@ as well as D@sub it@ value indicates that the plasma has induced a large amount of positive charges trapped in the bulk oxide and the interfacial defects in the SiO@sub 2@-Si interfaces. The trapped oxide charges are also the origin of the large V@sub fb@ shifts as well as the reduced @rho@@sub ox@. The observed charging damages have been found to be dependent strongly on the etching gases as well as the plasma conditions. The site-dependent variations of the charging damages were attributed to the non-uniform radial distribution of the charges on the oxide surfaces during the etching processes. A MOS capacitor was fabricated over the thin thermal oxide by employing the above plasma exposures during the poly-Si electrode and the subsequent pad etching to measure the changes in the gate oxide integrity (GOI) characteristics. Finally, we will quantitatively show that the leakage current of the thin gate oxide after the plasma processing is strongly related with the measured PDM results.

#### 9:00am PS+MS-WeM3 The Use of Simultaneous Modulation of Source and Wafer RF to Reduce Plasma Induced Damage, N. Hershkowitz, University of Wisconsin, Madison INVITED

A variety of different types of plasma phenomena can lead to plasma induced damage in the fabrication of small geometry devices. Oxide charging (probably the most significant source of damage), macroscopic and microscopic differential charging, over energetic ion beams, UV induced carriers and plasma etch induced silicon substrate roughness are some examples. In this paper, it is argued that simultaneous modulation of source and wafer RF in HDP tools provides a "control knob" for eliminating and/or reducing many of the sources of damage. Data are presented showing improvements resulting from simultaneous source and wafer (onoff) modulation. RF frequency and modulation duty cycle effects are discussed together with damage reduction mechanisms.

# 9:40am PS+MS-WeM5 Effect of Oxide to Nitride Etch Selectivity on Plasma Induced Charging Damage, *S. Ma*, *C. Björkman, R. Wang, L. Zhang, H. Shan,* Applied Materials Inc.; *R. Ramanathan,* Conexant Systems

Nitride layers are widely used for dual-damascene, self-aligned contact and border-less contact dielectric etch process as etch stop layers. It is also believed that such etch stop layer on top of metal electrode can also serve as plasma charging damage protection layer. This study shows no relationship between the dielectric to nitride etch selectivity and plasma induced charging damage. A Magnetically Enhanced Reactive Ion Etching (MERIE) chamber is used for this study with 0.25 um technology devices. In fluorine contained etching chemistry, strong recipe dependence on plasma charging damage is found regardless of the dielectric to nitride etch selectivity. A model of leaky nitride with charge built up on via hole bottom is proposed to explain the phenomena. In pure oxygen chemistry for in-situ polymer removal, plasma induced charging damage depends on the remaining nitride thickness. It is found that power is the most sensitive parameter than B-field, pressure, overetch and gas species to control damage. A mechanism is also proposed to explain the role of polymer formation and removal on top of nitride stop layer to plasma charging damage sensitivity

# 10:00am PS+MS-WeM6 Aspect Ratio Dependent Plasma-Induced Charging Damage in RF Pre-Cleaning of Metal Contact, J. Kim, K.S. Shin, W.J. Park, C.J. Kang, T.-H. Ahn, J.-T. Moon, Samsung Electronics, Korea

As the packing density increases in the fabrication of semiconductor, the aspect ratio and the CD (Critical Dimension) of a metal contact are exponentially aggravated in the dry etch process. The aspect ratio dependency on a plasma-induced charging damage during the RF precleaning of a metal contact has been evaluated with the two dimensional Monte-Carlo simulation and the related experiments. From the simulation of a metal contact opened on a gate metal, it is found that the potential on a metal contact bottom, which is directly related to plasma-induced charging damage, is saturated near 4 of aspect ratio after linearly increasing with the aspect ratio. However, the linear decrease of CD of a metal contact exponentially increases the potential stress on gate oxide. These simulation results are confirmed with the two different experiments, an in-situ charge-up monitoring and the electric test of a fully fabricated CMOS wafers. A phase-controlled inductively coupled plasma is proposed to suppress the plasma-induced charging damage. With the phasecontrolled inductively coupled plasma, the plasma-induced damage is strongly suppressed when the phase delay of the bias power to the source power is near 180 degree.

### 10:20am **PS+MS-WeM7 Real-time Observation of Relaxation of Disorderinduced Surface Stress**, *T. Narushima*, *N. Ueda*, University of Tsukuba, Japan; *A.N. Itakura*, National Research Institute for Metals, Japan; *T. Kawabe*, University of Tsukuba, Japan; *M. Kitajima*, National Research Institute for Metals, Japan

We present relaxation of disorder-induced surface stress. The surface stress changes on Si(100) were measured by means of an optical micromechanical cantilever technique. The samples were Si(100) cantilevers (450µm x 50µm x 2µm). They were treated by being dipped in 10% HF acid solution for 5 minutes, rinsed with deionized water for 5 minutes, and annealed at 1000K for 30 minutes in a UHV. To introduce disorder to surface, the surfaces were bombarded using an argon plasma with applying negative biases (-30V to -100V) at room temperature. Then, the disordered surfaces were oxidized using an oxygen plasma with applying positive bias (+45V), where the surfaces were subject to electron irradiation. We found a development of compressive stress on the Si surface due to defects produced by ion bombardment. This disorder-induced compressive stress was completely relaxed by the following plasma oxidation. The initial evolution of the surface stress during oxidation on the bombarded surfaces is guite different from that on unbombarded Si(100) surfaces. The disorderinduced stress was also relaxed completely by an exposure to argon plasmas under anodic conditions. The stress relaxation should be promoted not only by oxidation but also by electron irradiation. A possible mechanism of the stress relaxation is surface diffusion of Si adatoms via electron irradiation.

## Wednesday Morning, October 4, 2000

10:40am PS+MS-WeM8 Transient Charging Effects of Insulating Surfaces Exposed to a Plasma During Pulse Biased DC Magnetron Sputtering., E.V. Barnat, T.-M. Lu, Rensselaer Polytechnic Institute

The ability to control the charging of thin dielectric films exposed to ionized discharges, using a pulsed bias, is studied experimentally and theoretically. A dielectric film is exposed to the discharge and the transient currents associated with the dielectric's charging are measured after each pulse. Factors effecting the time scale the film undergoes charging, including the dielectric constant, the dielectric's thickness, the plasma density, and the amount of potential applied during each pulse are explored. By constructing a simple model based on the plasma's impedance to the pulsed bias and the capacitive coupling between the electrode and the surface of the dielectric where the charge accumulates, the observed transient currents are explained. Calculations are then made to determine the energy distribution of the ions extracted from the plasma and how both the pulse of the electrode and the charging of the dielectric influence the ion energy distributions. To demonstrate an application of the pulse bias technique, it is shown that we can dramatically control the film morphology and microstructure by pulse biasing the electrode. Also, by properly setting the pulse bias, the pulse frequency or the pulse duty, damage to thin dielectric films, such as electrical breakdown, is prevented during metallization.

### Plasma Science and Technology Room Exhibit Hall C & D - Session PS-WeP

#### **Poster Session**

PS-WeP1 Plasma Damage in Etching of SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Films Using Inductively Coupled Cl@sub 2@/Ar and Cl@sub 2@/N@sub 2@ Plasma, D.P. Kim, Chungang University, Korea; W.J. Lee, B.G. Yu, ETRI, Korea; T.-H. Kim, YIT, Korea; C.-I. Kim, Chungang University, Korea

In recent years, non-volatile ferroelectric random access memory (FRAM) has been attracted great attentoin for the applications with fast switching speed, low operating voltage, and high radiation hardness. FRAM comes to be used where high performance and power efficiency are required, in such as communication products, portable applications, logic IC, and smart cards. For highly density FRAM, one transistor and one capacitor structure (1-T/1-C) was proposed. Pb(Zr@sub 1-x@Ti@sub x@)O@sub 3@ (PZT), SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) and Bi@sub 3.25@La@sub 0.75@Ti@sub 3@O@sub 12@ (BLT) have been challenged as dielectric materials of capacitor. Among them, SBT thin films have been attracted because SBT thin films show high dielectric constant, long data retention and fatigue endurance up to 10@super 11@ switching cycles. A few papers have been reported about etching mechanism and damages during SBT thin film etching. Therefore, SBT thin films were etched in Cl@sub 2@/Ar and Cl@sub 2@/N@sub 2@ plasmas by performing measurements of etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy and secondary ion mass spectrometry. Higher etch rate was obtained in Cl@sub 2@/Ar plasma rather than in Cl@sub 2@/N@sub 2@. Atomic force microscopy (AFM) was used to investigate the surface morphology of etched SBT thin films. High-resolution transmission electron microscopies (TEM) and auger electron spectroscopy (AES) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current. Physical damages were more severe at high bias voltage and in Cl@sub 2@/Ar plasma rather than in Cl@sub 2@/ N@sub 2@. From the results, damages in etching of SBT thin films were due to ion bombardment. Low damages can be obtained at small ion mass and low bias voltage.

#### PS-WeP2 Design and Characterization of a Magnetic Pole Enhanced Inductively Coupled Plasma Source, T. Meziani, P.P. Colpo, F. Rossi, Joint Research Center, Italy

In the last decade, the ICs size shrinking has led to the development of a new generation of plasma source, enabling the generation of high plasma density with low ion energy: the Inductively Coupled Plasma sources (ICPs). ICP sources are widely used in semiconductor industry for their simple design, process flexibility and their high throughput. At present, the new challenge to be addressed is the scaling up of the plasma sources to enable large area specimen processing. Indeed, the semiconductor industry is now experiencing the transition from 200 to 300 mm wafer technology and plans the transition to 450 mm for 2010. On the other hand, the interest of the FPDs industry for larger area treatments is obvious for the flat video screen fabrication. The paper presents the design of a novel plasma source, enabling large area plasma treatment: the magnetic pole enhanced ICP (MaPE-ICP). The plasma source consists of a special arrangement comprising a special inductor embedded in a magnetic pole to create a concentrated and homogeneous magnetic field over large areas. We demonstrated that the plasma uniformity at laboratory scale (30cm) is better than the uniformity obtained with the classical ICP source on the same area. Furthermore, the obtained plasma characteristics (i.e. high densities of reactive species, low and controllable ion energy, wide pressure range) make the new source extremely promising for a whole range of processes such as large scale deposition, etching and plasma treatments. Finally, preliminary results of plasma density measurements over a large area MaPE-ICP reactor (1m x 1m) are presented.

#### PS-WeP3 Analysis of Chlorine-Containing Plasmas with Langmuir Probes, Self-Excited Electron Resonance Spectroscopy, and Optical Emission Spectroscopy, *G. Franz*, INFINEON Technologies, Germany; *P. Messerer*, Technical University, Germany

Capacitively coupled discharges of strongly reactive atmospheres, containing mixtures of boron trichloride and chlorine, are investigated employing spatially resolved Langmuir probe measurements, optical

emission spectroscopy, and self-excited electron resonance spectroscopy. The analysis covers the whole area spanned by these gases from pure boron trichloride to pure chlorine, discharge pressure over more than one magnitude, and RF power half an order of magnitude. Their impact is addressed on important plasma parameters like plasma density, plasma potential, electron temperature, electron collision rate with neutrals, and actual RF power coupled into the discharge. Since the methods are partially complementary, a mutual control of the obtained data is made possible. Whereas the concordance in electron plasma density is surprisingly good, the discrepancies in the determination of the electron temperature lead to the conclusion that the electron energy distribution must be described with two temperatures. Compared to discharges of inert gases, which are used as calibration standard, electron plasma density and electron temperature are both definitely lower, which is mainly caused by electron attachment of the electronegative molecules. Absolutely no chlorine could be found in the plasma which is referred rather to the effective cooling of the Clcontaining species than to the nonexistence of these species.

### PS-WeP4 Infrared Characterization of a Cascade Arc Plasma, *R. Raghavan*, *P. Morrison*, Case Western Reserve University

In-situ diagnostics of chemical vapor deposition (CVD) systems are limited in the mid-infrared (500-5000 cm@super-1@) region due to the lack of a high intensity light source. Noble gas cascade arc plasmas are potential high-intensity infrared light sources. We have constructed a argon cascade arc light source and characterized its infrared (2000-10000 cm@super-1@) emission properties using a Fourier transform infrared (FTIR) spectrometer. The properties of the plasma are adjusted by varying the pressure (1-4 atm) and the current (15-30 A) through the arc. To determine temperature from line emission of a plasma, the population distribution of excited states must be known. We show that our plasmas are in "partial local thermodynamic equilibrium" (PLTE) and use the Boltzmann equation to estimate excited state densities by assuming that only a fraction of the ground state Ar is in equilibrium with the excited states. This fraction as well as the plasma temperature are then regressed from a two-parameter least squares analysis of the measured infrared emission spectrum. Once we know the plasma temperature, we then estimate the electron density from continuum emission of the plasma. Alternately, we also estimate an electron density from the Saha equation. If the assumption of PLTE in our plasmas is valid, the electron densities resulting from these two techniques should be similar. Based on this observation, we find that the plasmas at the highest current (30 A) and pressures (3, 4 atm) satisfy the assumption of PLTE, while the plasmas at other conditions do not. This result enables us to calculate new transition probabilities for the infrared transitions in an Ar plasma. Plasma temperatures range between 9500-11500 K while electron densities are between 2-5x10@super22@ m@super-3@ for our plasmas. The total radiative power from the cascade arc is five times that of a conventional mid-IR light source like a globar and hence it is a feasible infrared light source.

#### PS-WeP5 Spatially Resolved Atomic Oxygen Concentration Measurements Using a Quartz Crystal Microbalance in a 300 mm Plasma Ash Chamber, *A.K. Srivastava*, *P. Sakthivel*, Eaton SEO

In a previous study, atomic oxygen (AO) concentrations have been measured in 200mm strip tools using a quartz crystal microbalance (QCM). This technique utilizes the resonant frequency of the crystals to monitor the mass gain of a silver film as it gets oxidized in an AO rich environment. Current work details similar results for high power plasma sources in a downstream 300mm dry strip tool. QCM data indicate that AO concentration is about 10@super 13@ per cubic centimeter under typical photoresist removal in 300mm systems. Data are presented on AO concentration sensitivity to varying process parameters like input gas mixture and chamber pressure. Additionally, correlation of AO concentration to photoresist strip rates on blanket-coated 300mm silicon wafers is made. Data indicate an increase in AO concentration as pressure drops, and a corresponding increase in resist removal rate. The effects on AO concentrations of using different showerhead configurations for uniformity in the chamber are also presented. By moving the QCM head within the chamber in the wafer plane, the spatial distribution of AO in the process chamber is mapped out. Finally, the use of an orifice on the QCM is shown to prevent overloading of the frequency counter, and a compensating transfer function may then be used to infer AO concentrations.

PS-WeP6 Plasma-Surface Diagnostics in LAPPS@footnote 1@, S.G. Walton, NRC Postdoctoral Research Associate; D. Leonhardt, D.D. Blackwell, D.P. Murphy, R.F. Fernsler, R.A. Meger, Naval Research Laboratory

In situ mass and energy resolved measurements of ion and neutral fluxes to a conducting electrode surface in NRL's Large Area Plasma Processing System (LAPPS) are presented. LAPPS uses a magnetically confined sheet of high-energy electrons to ionize a background gas, producing a high-density (10@super 9@-10@super 12@ cm@super -3@) planar plasma that is scalable to large areas (meters@super 2@). The electron beam is produced by a hollow cathode, embedded in a 100-300 Gauss magnetic field and injected into 20-200 mTorr of background gas. Hence, plasma production is decoupled from the reactor geometry, allowing independent positioning and biasing of electrode surfaces. The relative fluxes and energy distributions are reported for a grounded and rf-biased electrode and as a function of plasma-electrode separation. Ion and neutral species are sampled through a small orifice (sub-Debye length diameter) located in the center of the electrode and analyzed via an energy selector in series with a mass spectrometer. Relative fluxes and energy distributions are presented for discharges in Ar, O@sub 2@, Ne, and their mixtures over a range of conditions (pressure, mixture ratios). The results are discussed in terms of materials processing. Additional details concerning LAPPS and its processing applications are presented at this conference@footnote 2@. @FootnoteText@ @footnote 1@ Work supported by the Office of Naval Research. @footnote 2@ See presentations by co-authors at this conference.

#### PS-WeP7 Measurements of Plasma-wave Interactions in a Commercialscale Helicon-driven Plasma Processing Reactor, J.E. Norman, D.N. Ruzic, N. Li, M.E. Boaz, J.P. Allain, University of Illinois, Urbana-Champaign

Measurements of plasma-wave interactions in a commercial-scale helicondriven plasma processing reactor A Plasma Quest 256 research reactor powered by a PMT Mori 200 Helical plasma source has been used to study plasma wave interactions. Magnetically enhanced inductively coupled plasmas can operate in very different modes and operating regimes simply through external control. The ability to quickly change from one operating mode and plasma condition to another may allow the creation of multifunctioning processing environments: one machine that can replace many of the single-step chambers now required during semiconductor fabrication. To demonstrate this principle, Langmuir probe and spectroscopic measurements show that radically different plasmas can be produced through electrical and magnetic variation. Modeling has also been done which elucidates the physical mechanisms involved in the electromagnetic energy transfer to the plasma.

#### PS-WeP8 Spatial Profiles of Neutral, Ion and Etch Uniformity in a Large-Area High Density Plasma Reactor, *S. Yun, G.R. Tynan,* University of California, San Diego

The effect of ion and neutral uniformity on etch rate uniformity has been studied. In our experiments, the correlation between plasma conditions and etch uniformity has been measured in a large area high density plasma reactor. Spatial profiles of ion density, plasma potential, and radical density are measured across the face of a 20 cm wafer. Plasma profiles are measured by a Langmuir probe and radical density profiles are measured by an optical emission probe. Optical emission spectroscopy and spatial actinometry are used to calculate the spatial radical density on a wafer. As an initial experiment, we have performed the photo resist etching using oxygen plasmas. The results show that the spatial variation of etch rate is depend only on neutral profile when there is no applied substrate bias. The spatial variation of etch rate is depend on both neutral profile and ion flux profile when the bias voltage between -6 V and -100 V is applied on a substrate. The spatial variation of etch rate is depend on only ion flux profile when the bias voltage is below -100 V. These results are discussed including other effects such as spatial variation of wafer temperature. The results may suggest that ion uniformity may determine etch uniformity for processes which require significant energy sources from an energetic ion population (such as SiO@sub 2@ etching). Neutral reactant uniformity may determine etch uniformity for processes which do not require significant energy from ion energy (such as photoresist etching).

#### PS-WeP9 Probe Diagnostic Development for Electron-Beam Produced Plasmas, D.D. Blackwell, S.G. Walton, D. Leonhardt, D.P. Murphy, R.F. Fernsler, W.E. Amatucci, R.A. Meger, Naval Research Laboratory

The composition and distribution of particle species is the most basic in formation of a process plasma. Knowledge of the electron and ion energy distribution functions is prerequisite to obtaining accurate models of

plasma surface interactions and radical production. NRL has developed a Large Area Plasma Processing System based on electron beam ionization of gases.@footnote 1@ The LAPPS plasma source, having low electron temperature and low pressure, make it ideal for probe diagnostics. However, such measurements can become difficult due to the presence of large magnetic fields, RF biases on the processing surface, high energy electrons, and multiple ion species. We have developed probe diagnostics with an emphasis on overcoming these difficulties. RF compensation methods for Langmuir probes and resolution of distribution functions on RF timescales with specially designed energy analyzers allow us to measure instantaneous and time averaged plasma proper- ties, while increased digital resolution allows for more realistic representation of non-Maxwellian distribution functions. Magnetic based current diagnostics give us instantaneous readings of to process surfaces and relation to RF biases applied. For calibration and fine tuning of probes for the LAPPS machine, a test chamber (75 cm wide x 25 cm high) with a spiral RF antenna coupled to the plasma through a glass window was used. Langmuir probes, temporally resolvable ion and electron energy analyzers, and capacitive probes were used to investigate the bulk plasma characteristics. Comparisons between the effectiveness of different probe diagnostics and correlations to other in situ diagnostics such as mass spectrometry, microwave transmission, and optical spectroscopy methods will be presented. @FootnoteText@ @footnote 1@ See presentations by co-authors at this conference.

#### PS-WeP10 Langmuir Probe Measurements in an Inductively Coupled Ar/CF@sub 4@ Plasmas, M.V.V.S. Rao, M. Meyyappan, S.P. Sharma, NASA-Ames Research Center

Technological advancement in the microelectronics industry requires an understanding of the physical and chemical processes occurring in plasmas of fluorocarbon gases, such as carbon tetrafluoride (CF@sub 4@) which is commonly used as an etchant, and their mixtures to optimize various operating parameters. In this paper we report data on electron number density (n@sub e@) temperature (T@sub e@) ion energy distribution function (EEDF), mean electron energy, ion number density (n@sub i@), and plasma potential (V@sub p@) measured by using Langmuir probe in an inductively coupled 13.56 MHz radio frequency plasmas generated in 50%Ar:50%CF@sub 4@ mixture in the GEC cell. The probe data were recorded at various radial positions providing radial profiles of these plasma parameters at 10-50 mTorr pressures and 200 W and 300 W of RF power. Present measurements indicate that the electron and ion number densities increase with increase in pressure and power. Whereas the plasma potential and electron temperature decrease with increase in pressure, and they weakly depend on RF power. The radial profiles exhibit that the electron and ion number densities and the plasma potential peak at the center of the plasma with an exponential fall away from it, while the electron temperature has a minimum at the center and it increases steadily towards the electrode edge. The EEDFs have a characteristic drop near the low energy end at all pressures and powers, and their shapes represent non-Maxwellian plasma and exhibit more like Druyvesteyn energy distribution.

#### PS-WeP11 Target Surface Modifications during Reactive Sputtering of Aluminium in an Argon-oxygen Plasma, D.J.M.G. Depla, R. De Gryse, University Ghent, Belgium

The target voltage of an aluminium target changes during magnetron sputtering when oxygen is added to the argon plasma. This target voltage alteration has been ascribed to a target surface modification, which alters the ion-induced secondary electron emission (ISEE) coefficient. As most models assume that the target surface modification is induced by chemisorption of oxygen on the aluminium target, we have measured the influence of chemisorption on the target voltage. At low oxygen exposure an absolute target voltage increase was noticed. Extending the oxidation period resulted in an absolute target voltage decrease. Comparing these results with the measurements performed regarding reactive sputtering. we came to the conclusion that chemisorption cannot explain the target surface modification during reactive sputtering. Indeed, stability experiments of the target surface modification induced by reactive sputtering clearly indicated that the target voltage gradually changes towards the value measured for a target fully oxidized by chemisorption. This shows that the target surface modification during reactive sputtering is not the formation of a stable surface compound by chemical reaction between oxygen molecules and the aluminium surface as noticed during chemisorption. The chemical reaction between implanted reactive gas atoms and the target atoms forms the basic idea of the presented approach to describe the target surface changes.

PS-WeP12 An Investigation of Plasma-polymer Interactions by Mass Spectrometry, J. Hong, M.R. Wertheimer, L. Martinu, Ecole Polytechnique Montreal, Canada

Modification of polymer surfaces by low pressure plasmas has gained industrial importance for controlling adhesion of coatings, wettability, printability and other surface-related properties. However, relatively little is known about the complex interactions of plasma with polymer surfaces. The present study is designed to investigate these interactions by mass spectrometry : in a special plasma reactor, which can be excited by microwave (MW, 2.45GHz), radiofrequency (RF, 13.56MHz), or dual (MW/RF) frequency power, polymer specimens are placed directly on the electrode, which also contains a small inlet-orifice (100 micron diameter) into the Hiden EQP 1000 plasma monitor/quadrupole mass spectrometer/ion energy analyzer. We observe molecular fragments from various polymers (polyethylene, polypropylene, polvethylene terephthalate, etc), which are liberated by chain scissions provoked by various energetic plasma constituents (ions, radicals, ultraviolet photons, etc). The different plasma modes mentioned above, and the choice of plasma gas (inert or molecular gases) allow us to select the dominant plasma species, their energies and fluxes during these surface treatments. Finally, we can study the desorption kinetics of species diffusing from beneath the polymer surface, which are created by UV irradiation.

**PS-WeP13 Comparing Polyatomic Ions and Plasmas for Organosiloxane Film Growth from HMDSO**, *E.R. Fuoco*, *L. Hanley*, University of Illinois at Chicago; *A.J. Beck*, The University of Sheffield, UK; *P.N. Brookes*, The University of Sheffield, UK, United Kingdom; *R.D. Short*, The University of Sheffield, UK

Mass spectrometric sampling has found that large polyatomic ions are formed during plasma polymerization of hexamethyldisiloxane (HMDSO), implying that these ions could contribute to polymerization at the surface. This study uses mass spectrometric sampling to detect these ions in a low power HMDSO plasma. Adjacent work employs mass-selected beams of 15 - 100 eV Si@sub 2@O(CH@sub 3@)@sub 5@@super +@ ions to deposit organosiloxane films on Al surfaces. Monochromatic x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry are used to compare films formed from plasmas and those deposited from Si@sub 2@O(CH@sub 3@)@sub 5@@super +@ ion beams. These results support the argument that polyatomic ions and energetic neutrals play an important role in plasma polymerization.

#### PS-WeP14 Reactive Sputtering of Al@sub2@O@sub3@ in a Cylindrical Hollow Cathode Magnetron, A. Pradhan, D. Guerin, S.I. Shah, University of Delaware

Hollow Cathode Sputtering offers the advantage of 360-degree sputtering and allows the possibility to uniformly coat shaped articles, fibers and wires. We have studied the reactive deposition of Al@sub2@O@sub3@ using a hollow cathode sputtering process. A metal cylindrical target was used. Reactive sputtering process in a cylindrical magnetron is complicated due to redeposition of the sputtered flux. The control of the process is easier as it is relatively facile to pump to eliminate the unused reactive gas from a cylindrical magnetron than it is in the planar magnetron. We have characterized the reactive sputtering behavior of the Al metal target in Ar + O@sub2@ plasma. A hysterisis loop, typical of reactive sputtering, was obtained. The deposition rate, even in the poison mode, was high. This was perhaps due to the high pumping speed. The deposited film was also characterized by x-ray diffraction and x-ray photoelectron spectroscopy. The x-ray analyses revealed essentially pure metal films for low oxygen partial pressures. The pure metal to pure oxide transition, as the oxygen partial pressure in the sputtering gas was raised, was very slow. The transition region contained mixed valance aluminum. We will also present results on the optical and electrical characterization of the films.

#### PS-WeP15 High Rate and Low Damage Resist Ashing Employing Surfacewave Oxygen Plasma with High Permittivity Material Window, H. Shindo, K. Kusaba, Tokai University, Japan; K. Shinagawa, M. Furukawa, K. Kawamura, Canon Sales Corporation

Microwave plasma is one of candidates for large diameter plasma sources of the next generation. One issue in large diameter microwave plasma sources is on dielectric window material for microwave introduction. In this work, the microwave plasma production in a large diameter was studied employing a high permittivity window material. Especially, the plasma properties in O2 were examined in a viewpoint of the permittivity of the window material. If the microwave power is transferred into plasma in a surface wave mode, the plasma behaves depending on the permittivity of the window material. The plasma was produced in an aluminum chamber of 240 mm in diameter by introducing 2.45GHz microwave through a dielectric window of disc plate of 240 mm in diameter. Two kinds of dielectric materials, the quartz and alumina, were employed in this experiment and their permittivities were, respectively, 3.86 (14.9 GHz) and 9.7 (10 GHz), where the frequency used for the permittivity measurement was given in the parenthesis. The plasma parameters were measured by Pt plane probe of 1 or 0.5 mm in diameter in O2 plasma. The ashing rate of the photo-resist (PFI-58) was also measured at the substrate temperature of 200°. The results showed that the higher permittivity alumina window yielded two times higher electron density than the other in the regime above the cutoff of the microwave. Since the modes observed by the magnetic probe was consistent with the dispersion, it was concluded that the plasma production is due to the surface wave. The resist ashing experiments, which was performed in 8 inch wafer, showed that the rate was 2 times higher with the alumina than the other. A wafer damage was analyzed by both DLTS and carrier life time measurement, and it was concluded that a choice of the high permittivity window material provided one novel method for a large diameter wafer ashing processes with a high rate and low damage.

### PS-WeP16 Etch Issues for Trench First and Via First Dual Damascene, D. Keil, E. Wagganer, B.H. Helmer, Lam Research Corporation

Dual Damascene etch technology is emerging as a key enabler for advanced integration schemes. Chief among these is copper integration. However, Aluminum integration is also of great interest. Of the candidate methods for doing dual damascene, Trench First and Via First are the primary approaches typically considered. Several etch issues typically arise when implementing either of these approaches. The via first approach can lead to problems with either via veils or excessive faceting when the trench is etched. The trench first approach requires very high selectivity to the underlayer when it is desired to place vias both in and outside the trenches. In both cases, it is frequently desired to have no stop layer when etching the trench. This places stiff demands on etch uniformity, etch front control and sidewall profile angle control. Furthermore, after these structures are etched, one typically must open the underlayer layer (typically nitride) at via bottom without excessive perturbation to the structures already formed. The complexity of these issues makes it especially important to understand the etch mechanisms responsible for controlling these issues. A review of these issues is given and the current understanding of the relevant mechanisms are discussed.

#### PS-WeP17 Thermal Effects in Atomic-Order Nitridation of Si by a Nitrogen Plasma, *T. Seino*, *D. Muto*, *T. Matsuura*, *J. Murota*, Tohoku University, Japan

In atomic-order nitridation of Si(100) by a nitrogen plasma, thermal effects were investigated using an ultraclean ECR plasma apparatus. The Si substrate was cooled by being put on the suscepter which was cooled by liquid nitrogen with flowing He as a contact gas. Nitridation was performed at the N@sub 2@ pressure of 1.3-5.1Pa. In the initial stage of nitridation, the N atom concentration on the Si surface was normalized by the relative radical density and the nitridation with radicals proceeded according to Langmuir-type kinetics neglecting desorption. In this stage, the N atom concentration was almost the same in both the cases with and without cooling the Si surface. On the other hand, in the second stage where the nitridation of the deeper Si atoms below the surface was induced, the cooling caused suppression and saturation at nitridation. Therefore, without cooling Si surface, it is considered that the nitridation of the deeper atoms was enhanced by heating due to the ion incidence. The N atom concentration with cooling became higher at a lower pressure where the ion energy was high. Furthermore, in the cases of the Ar plasma exposure on Si in the same pressure as nitridation, it was found that the Ar atoms penetrate below Si surface and the Ar atom concentration becomes higher at a lower pressure. Therefore, the saturated N atom concentration may be determined by the ion energy. The exact Si surface temperature measurements in the nitrogen plasma are under investigation.

#### PS-WeP18 Ion Assisted Deposition of Silicon Nitride Films using Electron Cyclotron Resonance Plasma, *K. Denamma Vargheese*, *G. Mohan Rao*, Indian Institute of Science, India

Ion assisted deposition (IAD) is one of the most widely used techniques for the deposition of thin films. Electron cyclotron resonance (ECR) ion sources are ideal for ion assisted deposition due to high ionization efficiency even at low pressures. Silicon nitride films have been deposited by RF reactive sputtering with ion assistance from a ECR plasma. The ECR power was varied from 0 to 250 watts. The effect of ECR plasma on the growth of silicon nitride films has been shown to be systematic and is characterized

by using FTIR spectroscopy and Atomic Force Microscopy. The surface roughness for the films deposited without ECR plasma was about 2 nm and reduced to about 0.7 nm for those deposited with 250 watts of ECR power. Optical band gap studies also confirmed the effect of ion bombardment. The optical band gap changed from 2.2eV to 4.9eV as the ECR power is increased, indicating higher reactivity in the presence of ECR plasma. The optical transmittance of the films deposited with ECR assistance was good in the visible region reaching a maximum of 0.925 which is close to that of fused silica substrate used. Good quality silicon nitride films with a band gap of 4.9 eV, refractive index of 1.92 and extinction coefficient of 4x10@super -4@ have been obtained with a ECR power of 150 watts (corresponding ion density of 1.5x10@super 10@ cm@super -3@ on the substrate) and the surface roughness was less than 0.7 nm. Composition analysis carried out using Auger Electron Spectroscopy, showed a Si/N ratio of 0.76 for the films deposited under optimum deposition conditions.

**PS-WeP19 Structural Studies of Hyper-thin SiO@sub 2@ coatings on Polymers, G. Dennler**, Ecole Polytechnique de Montreal, Canada; A. *Houdayer*, University of Montreal, Canada; Y. Ségui, Université Paul Sabatier, France; M.R. Wertheimer, Ecole Polytechnique of Montreal, Canada

Transparent inorganic oxide coatings on polymers are playing an increasingly important role in pharmaceutical, food and beverage packaging. Such coatings are being prepared by physical-or by chemical vacuum deposition methods. They possess barrier properties when they are thicker than a certain critical thickness, d@sub c@; for d < d@sub c@, the "Oxygen Transmission Rate" (OTR, in standard cm@super 3@/m@super 2@/day/bar) is roughly the same as that of the uncoated polymer. This fact is commonly attributed in the literature to a "nucleation" phase of the coating, during which it is thought to present an island-like structure. In order to verify this hypothesis, we have deposited hyper-thin SiO@sub 2@ coatings on various flexible polymeric substrates (PET, PI, PP) using plasma-enhanced chemical vapor deposition (PECVD). The film thicknesses investigated here, well below d@sub c@ (typically in the range 1-15 nm), were determined by Rutherford Backscattering Spectroscopy (RBS), which allows us to determine the surface concentration of silicon. This was found to be a linear function of the deposition time, t, for t @>=@ 1 second. These results are compared with those from other thickness mesurements, namely spectroscopic ellipsometry, X-ray fluorescence, and transmission electron microscopy. Then, combining reactive ion etching (RIE) in oxygen plasma, scanning electron- and optical microscopy, we have been able to characterize the structure of the coatings : even for d @<=@ 2 nm, no island structure has been observed ; instead, we found continuous coatings which contain large concentrations, n, of tiny pinhole defects (with typical radii in the range of tens of nanometers), where n increases with decreasing d. These assertions are confirmed by grazing angle (80 degrees) XPS, which shows that even for d = 2 nm, the polymer substrate cannot be detected.

#### PS-WeP20 Numerical Study of HBr/O@sub 2@/CF@sub 4@ and HBr/O@sub 2@/CHF@sub 3@ Etching Chemistry in an Inductively Coupled Plasma Reactor, X. Xu, P. Schoenborn, LSI Logic Corporation

Inductively coupled plasmas (ICPs) have been developed for various applications in the modern integrated circuit manufacturing industry. One important ICP applicator for device fabrication is plasma etching of Si and other microelectronics materials because ICP reactors can produce high plasma density (10@super 11@ - 10@super 12@ cm@super -3@) at low pressure (a few to 10s mTorr). Increasingly stringent control of etching rates, profile shapes, and uniformity has led to using more complex chemistry mixtures in the selective etching of submicron features. There has been increasing interest in mixtures of HBr and fluorocarbons for etching of polysilicon and Si@sub 3@N@sub 4@ due to improved selectivity and superior control of the etched side wall profile. An understanding of the plasma chemistry is necessary and useful to examine plasma behavior from the source region to the substrate such as the fluxes of radicals and ions. In this study, we investigate the scaling of plasma chemistry mechanism of HBr/O@sub 2@/CF@sub 4@ and HBr/O@sub 2@/CHF@sub 3@ in an inductively coupled plasma reactor through a plasma simulation tool, the Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois. Addition of HBr into fluorocarbon plasmas cause significant reduction in F density. Results show that increasing gas pressure results in an enhanced Br flux and a diminished F flux in to the wafer. We will discuss the consequences of etching results of Si@sub 3@N@sub 4@.

**PS-WeP21 Low-temperature Deposition of Thin Oxides for Si-LSIs Using Electron Cyclotron Resonance Sputtering**, *T. Ono*, *K. Saito, Y. Taketa*, NTT Telecommunications Energy Laboratories, Japan; *S. Matsuo*, NTT AFTY Corporation, Japan

Electron Cyclotron Resonance (ECR) Sputtering has been investigated for application to Si-LSI processes of 8-inch wafers. The system consisted of the ECR sputtering process unit (with the ECR source coupled with divided microwaves).@footnote 1@ that was connected to an 8-inch wafer transfer system. For the deposition of aluminum oxides, the cylindrical sputtering target (Al: 99.99 %) was set around the plasma stream generated by ECR (gas: Ar/O@sub 2@). The sputtering was accomplished by biasing at 13.56 MHz rf utilizing ions in the plasma stream. The deposition was carried out without external heating; the wafer temperature during deposition was about 100 °C due to plasma heating. The film thickness ranged from 2 to 40nm. The uniformities of the deposited films were ±2.5 % (thickness), and ±0.3 % (optical refractive index of 1.61 at 632 nm) over a 200-mm-diameter. The resistivity and the brake-down strength of the 20-nm-thick films were about 5x10@super 14@ @OHM@cm, and 8 MV/cm, respectively. The dielectric constant was about 8. The fixed charge of the films depended on the oxygen partial pressure during deposition and can be controlled. ECR sputtering can be used for gate processes and capacitor processes at low temperature. @FootnoteText@ @footnote 1@ T. Ono et al., J. Vac. Sci. Technol. A12, 1281 (1994).

#### PS-WeP22 Silicon Etch Chamber and Process Development Using Diode Laser Measurements of HBr Concentration and Temperature, W. Collison, Lam Research Corp., U.S.A; T. Ni, Lam Research Corp.; S. Chou, J. Jeffries, Stanford University

Diode laser wavelength modulation spectroscopy technique developed by Stanford University@footnote 1@ has been used to measure HBr concentration and temperature in Lam 300mm TCP silicon etch chamber during blank poly silicon wafer etching. Various process conditions are measured. HBr concentrations as a function of pressure, gas flow, TCP power, bias power are recorded and correlated with etch rate data. HBr dissociation fractions are also measured before and after SF@sub 6@ waferless chamber clean with various focus ring materials including quartz, alumina, silicon nitride, silicon carbide. The results show that HBr dissociation fraction decreased 17% with the quartz focus ring after the chamber was cleaned by SF@sub 6@ plasma and about five wafers need to be processed before HBr signal gets to a steady level. Silicon carbide focus ring had essentially no influence on HBr concentration before and after chamber clean. Etch rate measurements show consistent results with HBr measurements. This suggests that using silicon carbide as focus ring material has certain advantages in poly silicon etch. It also shows that diode lasers can be used for real time control of plasma etch processes. @FootnoteText@ @footnote 1@ Shang-I Chou etc. "HBr concentration and temperature measurements in a plasma etch reactor using diode laser absorption spectroscopy", submitted to JVSTB.

#### PS-WeP23 Plasma Etching of Lead Germanate (PGO) Ferroelectric Thin Film, H. Ying, J.S. Maa, T.K. Li, F. Zhang, S.T. Hsu, Sharp Laboratories of America, Inc.

The lead germanate (PGO) thin film has been proposed for FRAM devices, especially for one transistor memory cell (1T) application. To realize such application, it is important to etch/pattern such thin film. In this work, plasma etching of PGO thin films was investigated by using chlorine or fluorine gas chemistries in an Electron Cyclotron Resonance (ECR) plasma reactor. Etch rates were studied as a function of etching conditions. The PGO etch rate of 600~650 Å/min was achieved by using a gas mixture of Cl@sub 2@ and Ar. In a pure Ar plasma, the PGO etch rate was significantly lower than that in a Cl@sub 2@/Ar plasma. The etching of silicon dioxide showed a similar trend under the same plasma conditions, however, the silicon oxide etch rate was much lower (~400 Å/min) than the PGO etch rate. In a CF@sub 4@/Ar plasma, the PGO etching behaves quite differently from the etching of silicon dioxide. While the silicon oxide etch rate increases with the CF@sub 4@ concentration, the PGO etch rate tapered off after the CF@sub 4@ concentration reached ~15%. In addition. similar to plasma etching of many other materials, the etch rate of PGO material increases as the RF bias power and/or the microwave power increases. The PGO etch rate decreases as the process pressure increases. Plasma etching induced damage to PGO thin film will also be discussed.

**PS-WeP24 Morphological Study of a New Copper Dry Etching Process**, *Y. Kuo, S. Lee*, Texas A&M University

Copper is the most desirable interconnect material for the high density VLSIC. Conventionally, it has been very difficult to etch copper using a parallel-plate plasma reactor under a mild condition, e.g., room temperature, low power density, etc., because reaction products, i.e., copper compounds, have low vapor pressures. Recently, the authors have published a new copper etching method based on a novel copper-plasma reaction.@footnote 1@ Instead of removing the reaction product during the plasma process, the copper film was consumed anisotropically and the copper compound was accumulated on the substrate surface. A solution was used to selectively dissolve the copper compound after the plasma process. The result shows that a high copper etch rate, e.g., > 3000 angstrom/min, could be achieved. The copper profile was adjustable with the plasma condition. In this paper, we are going to discuss the reaction mechanism of this new method under a large number of experimental conditions, such as feed gas, temperature, pressure, power, etc. The morphology change of the copper layer will be shown with SEM pictures. The physical and chemical analytical results of copper compounds will also be revealed. These results are critical to the understanding of this new copper dry etching process. @FootnoteText@ @footnote 1@Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188-L190, 2000.

#### PS-WeP25 Titanium-Nitride Etch Techniques Using High Density Plasmas for Advanced BiCMOS/CMOS Applications, *D. Galley*, ATMEL Corp., Fab 5; *K. Sannes*, Applied Materials Corp., COS; *A. Kelkar, G. Frazier, M.J. Evans, M. Whiteman*, ATMEL Corp., Fab 5

The multitude of uses for Titanium-Nitride(TiN) have become evident as the integration of system-on-a-chip applications has forced the film to be used in a variety of ways. The conventional uses of TiN have been as a top anti-reflection coating and a W-plug glue layer. Given it's relative thickness(e.g. 250 - 600 A on 5-8 kA of Aluminum), the plasma etch characterization of the film has been limited to breakthrough etch techniques which focus on the impact of the process on the underlying film(i.e. the Aluminum). In this study, the new applications of TiN for (1) Spacer/Encapsulation Technology for Line-On-Line Vias. (2) TiN/Nitride/TiN/Aluminum Capacitors, and (3) Metal Etch Stop Layers show the dramatic challenges for plasma etch techniques as the TiN films/sandwiches can become >3500 A in thickness. In this study using an Applied Materials DPS reactor, the impact of plasma chemistry choice(e.g. Cl2/Ar, SF6/Ar, CF4/Ar, C2F6/Ar), cathode temperature choice(i.e. the impact of cathode temperature on grain boundary etching/surface roughness), source RF power configuration(e.g. ramp-on/no ramp-on), and the choice of bias RF power are shown to be critical to realizing the device specific requirements of the process. The impact of the ratio of Titanium to Nitrogen in the TiN film impacts the final process result, as well. The process deliverables are: the ability to etch TiN and stop on Al, the ability to etch TiN and stop on/in thin layers of PECVD Nitride/Oxide, and the ability to control profile of the thick TiN. The etch responses(for a given application) result in a variety of subsequent electrical parametric effects(e.g. Via Resistance, Floating Gate Threshold Voltages, Capacitor Sidewall Leakages) which will be reviewed. Therefore, the choice of plasma parameters and the success of implementation directly impacts the ability to produce the intended integration objective of employing TiN for a large variety of uses in system-on-a-chip applications. For each given application, a family of processes will be proposed.

**PS-WeP26 Simulation of the Production of Atomic Hydrogen in a Lowpressure-arc-discharge-based Source**, *D.I. Proskurovsky*, Institute of High Current Electronics, Russia; *V.A. Kagadei*, Research Institute of Semiconductor Devices, Russia; *A.V. Kozyrev*, Institute of High Current Electronics, Russia; *I.V. Osipov*, Tomsk University of Control Systems and Radioelectronics, Russia

Treatment of semiconductor and metallic materials in atomic hydrogen is a promising method used in microelectronic and nanoelectronic technologies for desired modification of their properties at the surface, at interfaces, and in the bulk. To produce atomic hydrogen, dissociation of hydrogen molecules in the plasma of a gas discharge is often used. A quantitative model has been proposed which describes the gas discharge and the processes responsible for the production of atomic hydrogen in a cylindrical cell of an atomic hydrogen source based on a low-pressure arc discharge. At the first stage of simulation the principal plasma parameters (the electron and ion densities, the currents of ions, fast electrons, and plasma electrons) were calculated after which, based on the criterion for current self-sustaining, a calculation of the current-voltage characteristics (CVC's)

of the discharge was performed. At the second stage the rate of production of atomic hydrogen was calculated for different parameters of the discharge. The following mechanisms for the generation of hydrogen atoms were considered: impact dissociation of molecules by fast electrons accelerated in the cathode fall region, dissociation of the discharge column plasma by thermal electrons, and dissociation at the surface of a hot cathode. The spatial distribution of the atomic hydrogen flux onto the end wall of the discharge cell has been calculated. The calculated CVC's describe adequately the experimental relations obtained for wide ranges of discharge currents and hydrogen flow rates. This has made it possible to refine some constants of unit processes, such as the coefficient of secondary ion-electron emission, the average energy going into the formation of an electron-ion pair, and the temperature of the hot cathode. The atomic hydrogen yield was estimated by the intensity of the luminescent emission from a luminophor and with the help of a sensor based on a thin-film resistor. Comparison of experimental and theoretical dependences of the atomic hydrogen yield on the discharge current, the gas flow rate, and the position of the extraction hole suggests that the proposed model describes adequately the process of production of atomic hvdrogen.

#### PS-WeP27 Two-Dimensional Simulation of Pulsed Power Electronegative Plasmas, D.J. Economou, B. Ramamurthi, V. Midha, University of Houston

Low pressure electronegative plasmas are widely used for the fabrication of sub-micron semiconductor devices. Recently, pulsed power operation has emerged as a promising technique for reducing charge induced damage and etch profile distortion (e.g., notching) associated with conventional continuous wave discharges. This paper will report results of a 2-D fluid simulation of a pulsed-power inductively-coupled chlorine plasma. Simulation results show spontaneous separation of the plasma into an ionion core and an electron-ion periphery, depending on the negative ion to electron density ratio. The transition from an electron-dominated plasma to an ion-ion plasma in the afterglow was captured. The spatiotemporal evolution of the plasma for varying pressure, power, pulsing frequency and duty ratio has been studied. The evolution of negative ion density profiles is especially complex due to the formation of self-sharpening fronts during plasma "on" and subsequent back-propagation of the fronts during the plasma "off" stage of the pulse. Reactor geometry has a strong influence on negative ion evolution.

#### PS-WeP28 Kinetic Modeling of High-Density Diamond Deposition Plasma Chemistry, R. Blumenthal, Auburn University, usa

The chemistry of electron cyclotron resonance (ECR) microwave plasmas capable of diamond film deposition has been modeled using only neutral molecule energetics under the assumption that the plasma serves only as a constant source of hydrogen atoms. Supersonic pulse, plasma sampling mass spectra of 2% ethane in hydrogen and deutrium, 2% ethylene in hydrogen and deuteruium, 2% acetylene in hydrogen and deuterium and 4% methane in hydrogen and deuterium plasmas all have been fit with a single set of four physically realistic plasma conditions that were the only variable parameters in the modeling. The results of the calculations indicate that the primary reactive chemistry of C@sub 2@H@sub X@ species is the stripping of hydrogen from the hydrocarbons to produce acetylene, C@sub 2@H@sub 2@, which then undergoes closed-cycles of H(D) atom addition and abstraction for the balance of the species's lifetime in the plasma. The abstraction is the result of two-body collisions of the hydrocarbon with H(D) atoms generated by the plasma, while the addition is by a three-body collision, which is not observed (either experimentally or in modeling) for species other than acetylene. The notable exception is the ethane radical, C@sub 2@H@sub 5@, which in addition to the stripping chemistry, may react with H(D) atoms in a two-body collision to produce two methyl radicals, CH@sub 3@. Recombination of the methyl radicals is found to occur through the three-body reaction that produces ethane, C@sub 2@H@sub 6@. In deuterium plasmas, the resulting ethane is isotopically labeled and is responsible for the deuterated ethylenes observed only in the ethane and methane plasmas.

#### PS-WeP29 Evaluation of the Spatial Density of Sputtered Particles with Monte Carlo Simulation, *T. Nakano, S. Baba*, Seikei University, Japan

We have developed a method to evaluate the spatial density of sputtered particles in the sputtering process using Monte Carlo simulation. With the simulation, the elapsed time T@sub p@ of the particles (~10@super 5@ of trials) staying in a certain spatial region is summed up. In the same simulation, the time T@sub s@ required to emit all the trial particles is also calculated, by comparing the simulated arrival number of particles at the substrate with the deposition rate in the actual experiment. The number of

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particles in the spatial region can be obtained by taking the ratio T@sub p@/T@sub s@, and the spatial density is calculated by dividing it with the volume of the region. For the accurate calculation of T@sub p@, we have applied the model of the particle transfer in the gas atoms of Maxwellian distribution, which has been used successfully for the high pressure sputtering.@footnote 1@ In the present report, the calculated spatial density of the sputtered Cu is applied to explain the intensity of the optical emission from Cu in the plasma, because we have observed a different behavior in the pressure dependence between the emission at 324.8 nm and the emission at 510.6 nm in our previous report@footnote 2@. For gas pressures of 2~20 Pa and the deposition rate of 0.1~0.2 nm/s, the spatial density of the Cu atoms is found to be 10@super 17@~10@super 19@ m@super -3@ near the target. The density increases with the increase of the Ar pressure. This high spatial density of Cu atoms results in the selfabsorption of 324.8 emission by those atoms at the ground state, which makes the increase of 324.8 line less steeper than the 510.6 line at higher pressures. @FootnoteText@ @footnote 1@ T. Nakano, I. Mori and S. Baba, Appl. Surf. Sci. 113/114 pp.642 (1997) @footnote 2@ T. Nakano and S. Baba. Vacuum in press.

#### PS-WeP30 An Analytical Solution to a Langmuir- Hinshelwood Surface Model of Si Dry Etching, K.R. Milkove, IBM T.J. Watson Research Center

This talk describes a Langmuir- Hinshelwood phenomenological surface model for the etching of a Si wafer in a low pressure, high density SF@sub 6@ discharge. The model yields an analytical solution, and its methodology is applicable to any etch system in which the dominant etch component is ion-enhanced energy-driven. Such systems exhibit first-order adsorption kinetics. As such they are characterized by an etching rate that is linear with respect to the feed gas flow rate at low values and nearly independent of flow rate at high values. The key to this model is the derivation of an analytical expression for the surface coverage of the Si wafer by an incoming flux of neutral atomic F. It is shown that when the system pressure is controlled by a variable position throttle valve, the surface coverage is a dependent variable of the total pressure, the feed gas flow rate, the surface area of the Si wafer, the F on Si reaction rate constant (k@sub r@), the temperature of the F neutrals within the plasma discharge, the F mass, and the F to Si, S to Si , and Si to Si sticking coefficients. All of these variables are treated as being independent except k@sub r@, which is defined as a function of source power, bias power and the Si-Si bonding energy. Analytical expressions are derived for the Si etch rate, the particle residence time, the partial pressure of neutral atomic F, and the effective pumping speed. A major observation of this model is the realization that k@sub r@ can be determined by equating the partial derivative of the Si etch rate equation with respect to feed gas flow rate to the slope of the linear portion of the experimental Si etch rate versus feed gas flow rate data.

PS-WeP31 Plasma Measurements and Simulations of a New Hollow Cathode Magnetron Plasma Source for Ionized PVD of Cu Seed Layers, D.B. Hayden, M. Ow, K.A. Ashtiani, K.F. Lai, K. Levy, Novellus Systems, Inc. A commercial Hollow Cathode Magnetron (HCM) plasma source is used for depositing ionized Physical Vapor Deposition (PVD) copper (Cu) seed layers onto 200 mm wafers. Langmuir probes, an ion energy analyzer, and a deposition rate monitor are used to characterize the HCM plasma. Spatial scans of the downstream plasma regime, including near the wafer surface, are taken to measure the plasma densities, temperatures, and fluxes. Ionization levels, which greatly affect step coverage and uniformity, are analyzed versus different magnetic field arrangements. It is shown that the magnetic field arrangement near the cup-shaped target opening significantly affects the electron confinement in the source; thus the ionization levels of both argon working gas and sputtered copper. Based on the findings, improvements in the HCM source will be discussed which result in the ability to precisely control the ionization levels in the source as well as the uniformity of the arriving ion flux at wafer level. These improvements yield a 10-50% improvement in the Cu seed step coverage and a 10x improvement in deposited Cu uniformity. Sheet resistance and film thickness uniformities of <1% are achieved across a 200mm wafer. In addition, bottom coverages of 25% and 50% are achieved in 0.25um, 5:1 aspect ratio vias and trenches respectively. The plasma characterization results will be presented and compared to simulations from the Hybrid Plasma Equipment Model (HPEM).

PS-WeP32 New Reactor for High-rate Deposition of Functional Coatings on Polymer Substrates, *P. Bulkin, A. Hofrichter, B. Drevillon,* LPICM, Ecole Polytechnique, France

Concept of Multi-Magnetron Electron Cyclotron Resonance (MMECR) reactor was developed for applications in high-rate low temperature deposition of SiO@sub 2@/SiO@sub X@/Si@sub 3@N@sub 4@ multilayer and gradient films onto large area polymer substrates, flat and bended. Whereas broadly used electron beam evaporation and magnetron spattering techniques well suited and extensively used for multiplayer coatings, CVD and PECVD in particular do have clear advantages for gradient films deposition. We present an efficient concept of plasma reactor and report on process parameters. Flexible coaxial cables deliver microwave power to 25 magnetron applicators wich contain rare-earth NdFeB permanent magnets. Gas injection arranged through two distribution grids, one for silane and one for other gases, respectively. In the current version the system provides uniformity of better than 2 per cent on area of 35 cm in diameter (with magnetron antennas arranged in 30x30 cm plane and facing substrate) for both silica and silicon nitride films. Maximal growth rate obtained without compromising the quality of material is up to 6 nm/sec for SiO@sub 2@ and 1 nm/sec for Si@sub 3@N@sub 4@. Films are found to be dense and have good adhesion to polycarbonate.

### Plasma Science and Technology Room 310 - Session PS1+MS-WeA

### Sensors and Control in Plasma Processing

Moderator: I.P. Herman, Columbia University

2:00pm PS1+MS-WeA1 Supervision of Plasma Processes using Multiway Principal Component Analysis, D. Knobloch, F.H. Bell, Infineon Technologies AG, Germany; K. Voigtlaender, J. Zimpel, Fraunhofer Institute IVI, Germany

In modern IC-manufacturing lines, plasma processing is still one of the most complex single process steps. The trend towards even smaller feature sizes and greater wafer diameters results in the need of better process and equipment control. In previous studies@footnote 1,2@, we have shown that an OES-system, based on a multiband CCD-spectrometer and operated with a home built software, can be used for run-to-run and real time process control. In this work, we show how we extended our software tool in order to improve data analysis. A MPCA (Multiway Principal Component Analysis) has been implemented that allows extraction of key numbers from spectral data simultaneously in time and wavelength. Key numbers are extracted for single processes as well as for run-to-run variations. As an example, the chamber conditions as a function of rf-hours and process mix is characterized by MPCA key numbers. It is shown, that the key numbers represent the cleanliness of the plasma chamber that depends on the process mix. Consequently, the key numbers can be used to establish an optimum product flow in the chamber in order to optimize wet clean cycles and control particle generation. Furthermore, we demonstrate, how fault detection, such as determination of gas flow variations or chamber leaks, can be achieved. The MPCA key numbers of misprocessed wafers show variations to processing of good wafers and can be correlated to certain equipment or process faults. However, the establishment of a catalogue with spectral pattern of fault classifications, such as chamber leaks, is needed. Consequently, preventive maintenance is triggered in order to fix the observed equipment faults as soon as possible. @FootnoteText@ @footnote 1@ D. Knobloch et al, November 1998, AVS 45th International Symposium, Baltimore @footnote 2@ D. Knobloch et al, October 1999, AVS 46th International Symposium, Seattle

#### 2:20pm PS1+MS-WeA2 Sensors and Control in Plasma Processing, J.C. Arnold, M.J. Hartig, C.F. Pfeiffer, J.A. Rivers, M.L. Johnson, Motorola Semiconductor Products Sector INVITED

Even with the entrance of such processes as CMP and electrochemical deposition into the mainstream of semiconductor manufacturing, plasma processes remain among the most complex processes in the fab as well as among the most difficult to sustain. Furthermore, plasma deposition, etching, and cleaning processes are so numerous in typical product flows that the potential economic impact of plasma tool or process breakdowns is tremendous. The impetus for application of advanced sensors and automatic controls to these processes has been clear for years; however, widespread deployment of these devices and techniques in high volume manufacturing has been elusive. In this presentation, we will examine reasons for the apparent weakness in the pace at which sensors and controls have been adopted. We will begin with consideration of the terms "sensor" and "control" as related to the current state of the art in plasma processing. We will evaluate some of the sensor and control industry's current offerings in the context of the sensor and factory CIM system's ability to provide the "Acquisition - Analysis - Action" chain of three characteristics which we believe to be essential for adding value in the manufacturing environment. Finally, we will offer some end user perspectives on how changes in the business relationships between sensor and software vendors, capital equipment suppliers, and device manufacturers would facilitate more rapid and effective transfer of new techniques from the research lab to the production floor.

# 3:00pm PS1+MS-WeA4 Run-to-Run and Real Time Process Control of Plasma Processes using an Inductive Antenna with Microsecond Resolution, J. Mathuni, F.H. Bell, D. Knobloch, Infineon Technologies AG, Germany

Equipment and process stability during the fabrication process of integrated circuits is one of the main issues in current and future production lines. This is particularly mandatory for plasma processes. Intelligent run-to-run and real time control using plasma sensors help to prevent wafer scratches or misprocessing and to monitor chamber drifts, e.g. caused by damaged reactor walls or polymer coating on chamber walls

during wet cleans. We have implemented the real time control of plasma processes using an in house developed antenna that measures the electric field of the plasma with microsecond resolution. Introduction of this sensor in our fabrication lines was challenged by two factors, namely, the development of robust and low cost hardware and easy to use software including process and equipment related control algorithm. The latter needs special attention, since the time resolution in the range of microseconds results in a very high amount of data making intelligent data reduction techniques mandatory. The measurement technique requires a dielectric material between plasma and sensor that can be easily realized using the quartz endpoint window of the plasma chamber. The benefit of this sensor is demonstrated for applications such as arcing detection, a phenomenon that may occur during microseconds and results in yield killing particle generation, and process parameter dependencies, such as Bfield and power analysis. As a result, preventive maintenance is automatically triggered by sensor data. Since the sensor allows electric field measurements with nanosecond resolution, analysis of pulsed plasmas could be a further application.

#### 3:20pm PS1+MS-WeA5 Improved Utility of Microwave Energy for Semiconductor Plasma Processing through RF System Stability Analysis and Enhancement, *P.W. Rummel*, *T. Grotjohn*, Michigan State University, US

The bulk of today's semiconductor plasma processing equipment utilizes RF energies at frequencies from 50 KHz to 60 MHz for deposition, etching, cleaning and various other processes. One of the impediments to utilizing microwave energy for these processes is the inherent instability often encountered with systems operating at frequencies of .5 to 2.45 GHz. Systems with plasma loads excited by resonant antennas, impedance matched by resonant circuits or cavities, and powered by generators of various source impedances are invariably unstable over some operating conditions. For microwave systems, this instability typically manifests itself as a propensity for the plasma to extinguish or rapidly change to a lower density as the impedance matching device is adjusted to minimize reflected power to the microwave generator. This paper shows why this instability exists and how a microwave driven plasma system can be modified to achieve better stabilization. A Matlab Simulink model and a state-model control analysis are used to identify system parameters that affect system stability and to predict the results of modifying those parameters towards the goal of improving stability. A plasma system utilizing a microwave cavity plasma reactor operating at 2.45 GHz. is first characterized to develop the models, and then modified to improve stability and illustrate the models' predictions. A high correlation between predicted and measured system stability validates the method of using a control analysis to model plasma system stability.

3:40pm PS1+MS-WeA6 Modeling and Real-time Control of RF Diode Sputtering for GMR Thin Film Deposition, S. Ghosal, R.L. Kosut, J.L. Ebert, L. Porter, SC Solutions, Inc.; D.J. Brownell, Nonvolatile Electronics, Inc.; H.N.G. Wadley, University of Virginia, usa

This presentation describes the development and implementation of realtime control of rf diode sputter deposition resulting in significantly reduced wafer-to-wafer variation in device properties. Giant magnetoresistive (GMR) materials have very important applications which include technologies such as hard disk read-heads, computer memory, and sensors. One common configuration for thin-film sensors made by NVE is the GMR multi-layer consisting of sixteen metallic layers with individual layer thickness ranging from 15 to 40 @Ao@. For maximum GMR, the acceptable variation in layer thickness from one deposition cycle to another is very small (0.5 @Ao@ for the critical CuAgAu conducting layer). Before this work, there was considerable variation in GMR properties from wafer to wafer, despite no change in the nominal values of layer thickness. Sensitivity studies using a steady-state physical model (integrating plasma, sputter and atom transport processes) showed deposition thickness falling out of acceptable range with relatively small changes in rf power, chamber temperature, pressure, and electrode spacing. Careful experiments showed that while three of the four variables were controlled relatively well, there was significant variation (>1%) in total rf power delivered due to transients at the onset of the plasma. A controller was designed to compensate for transient fluctuations by turning off the plasma based on the timeintegrated DC bias voltage at the target. This approach keeps the total rf energy input into the plasma constant for individual layers deposited. As a result of implementing this controller, the standard deviation (wafer-towafer) in average GMR % and in sheet resistance were both reduced by more than half. Additionally, guided by the integrated physical model,

within-wafer uniformity was considerably improved by optimal electrode spacing and target shaping.

4:00pm PS1+MS-WeA7 Productivity Solutions for Eliminating Within-Wafer and Wafer-to-Wafer Variability in a Silicon Etch Process through Plasma and Surface Diagnostics, *E.A. Edelberg*, *L.B. Braly*, *V. Vahedi*, *J. Daugherty*, Lam Research Corporation; *S.J. Ullal*, *A.R. Godfrey*, *E.S. Aydil*, University of California, Santa Barbara; *H.K. Chiu*, *H.J. Tao*, Taiwan Semiconductor Manufacturing Corp.

Various plasma and surface diagnostics were used to understand the root causes that lead to within-wafer and wafer-to-wafer variability in critical dimension (CD) loss in Si etch applications. It is found that the conditions of the reactor walls can play a significant role in determining the plasma properties and therefore the figures of merit of the etching process. Etch products from the wafer can adsorb and build up on the walls of the chamber leading to changes in the wall properties. These changes can lead to drifts in the plasma properties and cause wafer-to-wafer variability of the etch process. It is demonstrated that such drifts can be avoided by cleaning the walls of the reactor using Fluorine-containing plasmas in between wafers. We demonstrate that a fundamental understanding of the chemistry and composition of the deposited materials on the walls of the chamber and their relation to the gas phase species can be used to develop and optimize appropriate reactor wall cleaning processes. A multiple pass downstream Fourier transform infrared (FTIR) spectrometer is used to quantitatively measure the concentration of gas phase species such as SiCl@sub 4@ and SiF@sub 4@ in the reactor exhaust. In addition, a novel diagnostic technique based on the principles of multiple total internal reflection FTIR spectroscopy is used to measure, in situ, the presence and composition of material deposited or removed from the walls of the chamber. In particular, during Si etching processes with Cl@sub 2@/O@sub 2@ plasmas, the deposited films were found to be the byproducts of the etching reactions and contain Si, O and Cl. We show that performing a short plasma chamber clean with the appropriate chemistry between each wafer can reduce the wafer-to-wafer variability of both etch rate and CD bias. By performing an in situ clean after every wafer during a 0.13 micron gate etching process the wafer-to-wafer repeatability is reduced to 2nm (at 3 sigma).

4:20pm PS1+MS-WeA8 Source Optimization for Magnetron Sputter-Deposition of NbTiN Tuning Elements for SIS THz Detectors, N.N. Iosad, Delft University of Technology, The Netherlands; B.D. Jackson, J.R. Gao, Space Research Organization of the Netherlands; S.N. Polyakov, Moscow State University; P.N. Dmitriev, Russian Academy of Sciences; T.M. Klapwijk, Delft University of Technology, The Netherlands

NbTiN is one of the most promising materials for use in the tuning circuits of Nb-based superconductor-isolator-superconductor (SIS) mixers for operating frequencies above the gap frequency of Nb (about 700 GHz). Device development requires stable and reproducible film properties. In this manuscript we compare the properties of NbTiN and NbN films obtained with a DC magnetron sputtering source using balanced and unbalanced magnetic trap configurations. This experiment shows that reducing the effectiveness of the magnetic trap by changing the magnet configuration is equivalent to reducing the sputtering pressure from the prospective of the film properties. We find that the properties of the films are not stable throughout the target life-time. Sputtering source with balanced configuration shows degradation of the NbN film properties as the target gets grooved for the fixed applied power and sputtering pressure. In contrast unbalanced sputtering source shows opposite behavior for the NbTiN films. We also show that it is possible to optimize the configuration of the magnetron magnets to produce stable and reproducible NbTiN films under the same gas pressure and applied power throughout the target lifetime.

#### 4:40pm PS1+MS-WeA9 Multiwavelength In-Situ Ellipsometry for Optical Coatings Fabrication: Optimal Control Strategies and Results, A. Hofrichter, D. Kouznetsov, P. Bulkin, B. Drevillon, Ecole Polytechnique, France

There is an increasing interest in adopting ellipsometric control for the manufacturing of optical filters. Ellipsometry does not relay on the amplitude of reflected signal, has very high sensitivity to both, thickness and complex refractive index, and can be used directly to probe growing surface, thus it is neither limited to transparent films nor depends on stability of light source. In comparison with such traditional techniques, as quartz crystal monitor and transmission/reflection spectrometer or laser interferometer, it is free of most their problems. However, interpretation of ellipsometric data is much more complicated and usually prevents

application of ellipsometers for real-time process control in industrial environment. We present a robust algorithm for feed-back control of the PECVD deposition, based comparison of pre-computed ellipsometric trajectories with real-time data stream. Such approach allows to stop growth of each layer with high accuracy without performing complicated real-time inversion of ellipsometric data. Using our Integrated Distributed Electron Cyclotron Resonance (IDECR) PECVD reactor we performed depositions of multilayer and gradient optical coatings with good agreement with design. The next step will be inclusion of dinamic corrections of gas flows based on real-time determination of refractive index profile.

#### 5:00pm PS1+MS-WeA10 Low Open Area Endpoint Detection of Plasma Etching Processes - Limitations and Signal to Noise Characterization, *B.E. Goodlin*, *D.S. Boning*, *H.H. Sawin*, MIT; *M. Yang*, Texas Instruments, Inc.

In low open area contact and via etches, endpoint detection has proven very challenging in manufacturing, despite apparent successes in research and development. In our current studies, we are looking into critical issues preventing successful implementation of endpoint detection in a manufacturing environment. In particular, we have characterized two major limitations to endpoint detection inherent in many oxide etching processes. 1) Wafer Edge Limitations - Depending on processing conditions, the wafer edge contributes between 1% to 6% open area to the etch, and thus cannot be neglected in the endpoint detection scheme for etches where the patterned area is <10% open area. 2) Interferometry Limitations - When using optical emission spectroscopy, reflections from the wafer surface and the top electrode can lead to a significant source of noise that is very difficult to remove and can easily lead to false identification of endpoint. In addition to looking at limitations inherent in typical processes, we have also guantitatively compared performance of various sensors that have been proposed for endpoint detection. S/N was characterized for 4 different levels of open area (100%, 20%, 0.7%, 0.14%) for optical emission spectroscopy (OES), residual gas analysis (RGA), and RF Impedance sensors. Our findings indicated that the RGA had the best S/N capability at 0.14% open area, but the simple monochromator OES system was a close second, with good capability at 0.7%. Lastly, we have compared performance of multivariate OES systems with single wavelength monochromator systems and found that the monochromator showed greater capability for low open area endpoint detection. After revisiting some of the multivariate algorithms, it was discovered that the S/N improvements previously claimed for multivariate algorithms have been overstated. In some cases multivariate algorithms can actually decrease S/N.

### Plasma Science and Technology Room 311 - Session PS2-WeA

#### **Feature Evolution**

Moderator: D.B. Graves, University of California, Berkeley

2:00pm PS2-WeA1 Undercut and Bowing Characterisation in High Aspect Ratio Trenches of Poly-Si Etched in an ICP Reactor using Cryogenic SF6/O2 Chemistry Process, *M. Boufnichel*, University of Orleans, CNRS, France; *S. Aachboun*, ST Microelectronics, France; *G. Marcos, P. Ranson*, GREMI, France

In the last few years, deep trenches in silicon obtained by plasma etching have been widely studied for MEMS and/or microelectronics applications. A cryogenic method with an SF6/O2 chemistry plasma in an Alcatel ICP reactor is used to achieve deep trenches with high aspect ratio (>10) and high anisotropy. The etching rate in 2  $\mu$ m wide and 100  $\mu$ m deep trenches is about 3.5µm/min. The slope of the trenches can be adjusted from 88° to 90° and selectivity is higher than 300. However, profiles need to be improved, mainly by reducing the undercut and the bowing effects. Undercut is a lateral etching occurring under the mask which enlarges the trench opening and bowing is a local lateral etching located on the sidewalls and resulting in profiles destruction. This study deals with improvements in these effects. We investigated the outcome of process parameters (pressure, bias voltage, temperature, oxygen flow rate) and mask characteristics (nature, thickness, side slope, trench width and length). We tested several more or less conducting masks: oxide, thermal oxide created from TEOS gas, PSG (Poly-Silicate Glass containing 4% of phosphor), Sandwich (one layer of Si between two layers of SiO2) and Al. The different mechanisms responsible for undercut and bowing are finally discussed and evaluated.

2:20pm PS2-WeA2 Origin of Sidewall Deposition during Cl@sub 2@/O@sub 2@ Etching of Sub Micron Features in Inductively Coupled Plasma Reactors, S.J. Ullal, A.R. Godfrey, E.S. Aydil, University of California, Santa Barbara; E.A. Edelberg, L.B. Braly, V. Vahedi, J. Daugherty, Lam Research Corporation

Shallow trench isolation (STI), a manufacturing technique used to isolate transistors in integrated circuits (IC), involves etching a trench of specific dimensions and shape into a silicon substrate in a high density inductively coupled plasma reactor. The trench is later filled with a dielectric and polished, resulting in a filled isolated shallow trench. To attain the best device characteristics, the filled trench must not contain any voids, which could be formed during filling, and avoided by engineering tapered sidewalls. These profiles are formed by redeposition of etch products on the sidewalls of the trench. The taper angle depends on a delicate balance between etching and redeposition on the sidewalls. In order to meet the stringent requirements of the IC fabrication industry, the taper angle on the sidewalls must be invariant to the position of the trench on the wafer and also be reproducible from wafer-to-wafer. To achieve these goals, a fundamental understanding of the nature and the origin of sidewall deposition is required. A typical STI etching process using Cl@sub 2@/O@sub 2@ gases was used to illustrate the dependence of sidewall deposition on chamber wall condition. A novel diagnostic method based on in situ multiple total internal reflection Fourier transform infrared spectroscopy was used to study the nature of the species deposited on the walls of the chamber. Etch products such as SiCl@sub x@ were detected by optical emission spectroscopy and Fourier transform infrared spectroscopy within, and downstream of the chamber respectively. Scanning electron micrographs of sub 0.25  $\mu m$  features were examined to determine the profiles after etching. Simultaneous monitoring of the etch products in the gas phase, on the reactor walls, and in the reactor exhaust provides evidence which suggests that the deposition on the sidewall occurs due to a direct flux of etch products leaving the trench, rather than redeposition from the gas phase.

# 2:40pm PS2-WeA3 Profile Simulation of Poly-Silicon Gate Features Etched with Cl2/HBr/O2 Plasmas, *L.B. Braly*, *D. Cooperberg*, *V. Vahedi*, Lam Research Corp.

The stringent requirements for line-width control during etching of sub 0.18-micron features for polysilicon gate applications demand a better fundamental understanding of the basic mechanisms that lead to linewidth variation. Several groups have proposed various mechanisms for sidewall deposition on etched profiles, as well as mechanisms for etching Si with Cl2/HBr/O2. We are using our feature profile simulator (along with diagnostics) to test various mechanisms. Measurements of ion flux and polysilicon etch rates under various conditions are used to determine polysilicon etch yields for Cl2 and HBr. The sidewall deposition model includes direct (line of site) and redepostion of etch products on the feature sidewalls. The validity of these mechanisms is tested by comparing predicted etched features against real etched features. The simulator is also calibrated using data from profile wafers and over-hang wafers. We will show comparisons between predicted profiles and etched profiles under conditions where line-width growth (CD gain) and line-width loss (CD loss) are observed.

#### 3:00pm PS2-WeA4 Feature Profile Evolution during Pulsed Plasma Etching: Effects of Redeposition of Time-Dependent Etch Products, *K. Ono, H. Kousaka*, Kyoto University, Japan

Pulsed plasma etching has recently been attracting much attention as an advanced processing technique in the fabrication of microelectronic devi ces. The inclusion of pulse repetition frequency and duty cycle provides us with additional control variables to optimize the plasma process. In contr ast to a relatively deep understanding of gas-phase chemical aspects of puls ed discharges and their effects on the processing, little work has been conc erned with time-varying surface chemistry therein. This paper is concerned with the surface chemistry and the resulting profile evolution during pulsed plasma etching of Si in Cl@sub 2@. The time-dependent behavior of surface chlorination and ion-enhanced desorption of neutral Cl atoms adsorbed as wel I as reaction products SiCl@sub x@ from the surface is calculated in pulsed operation, using a simple model based on Langmuir adsorption kinetics. The etched profile evolution is then simulated for infinitely long trenches with different widths, taking into account the transport of ions and neutrals in microstructural features: geometrical shadowing of the structure, reemissio n of neutrals at the surface on incidence, and also redeposition of etch pro ducts from the surface being etched. The product species desorbed is assume d to be time-dependent, owing to reaction layer dynamics of the ion-assisted

processes on a time-scale of micro to milliseconds: on a 1 ms time scale or shorter, tightly bound intermediates such as SiCl and SiCl@sub 2@ are relea sed by momentum of the impinging ions, having large sticking probabilities o n surfaces; on a time scale of tens of milliseconds and longer, the ion-enha nced formation of SiCl@sub 3@ and SiCl@sub 4@ is expected, having smaller st icking probabilities. The numerical results indicate that the effect of red eposition of etch products is more significant for pulsed discharges with sh orter periods and smaller duty ratios, giving outwardly tapered profiles whi ch are more pronounced on narrower pattern-width or higher aspect-ratio feat ures. These results will also be compared with experiments.

#### 3:20pm PS2-WeA5 A Model for Si Etching in an Inductively Coupled SF@sub 6@/C@sub 4@F@sub 8@ Discharge, S. Rauf, W. Dauksher, V. Arunachalam, P. Ventzek, Motorola Inc.; L. Lea, S. Hall, Surface Technology Systems, UK

Fluorine rich plasmas such as SF@sub 6@ are known to rapidly etch Si. However, due to inadequate polymerization in SF@sub 6@, it becomes difficult to anisotropically etch high aspect ratio features with straight sidewalls. Polymerizing gases such as C@sub 4@F@sub 8@ are therefore added, either directly in the SF@sub 6@ discharge or in a separate polymerization step, to obtain the desired etch profiles. To understand the dynamics of Si etching in SF@sub 6@/C@sub 4@F@sub 8@, an integrated equipment and feature scale model has been developed for these plasmas. The model is based on the Hybrid Plasma Equipment Model (HPEM) and Monte Carlo Feature Profile Model (MCFPM) from the University of Illinois. The gas phase chemical mechanisms for SE@sub 6@ and C@sub 4@E@sub 8@ are primarily based on electron impact cross-sections available in the literature. Judicious adjustments have however been made to match model predictions with experiments. The surface mechanism for SF@sub 6@ assumes reactive ion etching due to the combined effect of F and energetic ions. The C@sub 4@F@sub 8@ discharge can etch (due to the synergistic effect of ions, CF@sub x@ radicals and F) and deposit polymer (due to CF@sub x@ radicals). The equipment model has been validated using gas phase measurements while the feature scale model has been calibrated using etch/deposition rate measurements and comparing model predictions to etch profiles. Results show that the SF@sub 6@ plasma is quite electronegative with SF@sub 6@@super -@ and F@super -@ being the dominant negative ions. CF@sub 2@ is the primary CF@sub x@ radical in the C@sub 4@F@sub 8@ discharge, and it is the main precursor to polymer formation. The paper investigates Si etching in both a multi-step process (with separate etching and passivation steps) and a combined SF@sub 6@/C@sub 4@F@sub 8@ discharge.

# 3:40pm PS2-WeA6 An Integrated Model for Oxide Etch using Fluorocarbon Plasmas, V. Arunachalam, S. Rauf, P. Ventzek, T. Sparks, Motorola Inc.

Precise control of feature profile evolution during oxide etch using fluorocarbon plasmas is crucial to successful multilevel metallization. An important step in achieving this control is an understanding of the underlying physics and chemistry of the process across the various length scales ranging from the equipment scale to the feature scale, and their relationship to the equipment level knobs. This important step is captured through an integrated model comprised of an equipment scale model, a sheath model and a feature scale model. Using this model, the effect of typical process parameters on feature profile is examined in a generic inductively coupled plasma etching system. A surface chemistry mechanism developed using experimentally observed results is incorporated in the model. It includes processes such as polymer formation, ion assisted and thermal etching, ion sputtering and reflection, desorption and redeposition. The simulation results show the increase in anisotropy of the etch profile, decrease in the selectivity to the underlying silicon layer, and the transition from deposition to etch with increasing ion energy.

#### 4:00pm PS2-WeA7 Modeling of Trench Filling During Ionized Metal Physical Vapor Deposition@footnote 1@, J. Lu, M.J. Kushner, University of Illinois at Urbana-Champaign

Ionized Metal Physical Vapor Deposition (IMPVD) is used to deposit metal seed layers into high aspect ratio trenches in semiconductor processing. Conformal deposition and filling of trenches require an optimized ratio of neutral to ion flux, and optimized energy and angular distributions of the precursors. In this paper, we report on a reactor scale to feature scale computational investigation of Cu IMPVD in which this optimization is discussed. The computational tools used are the 2-dimensional Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Scale Model (MCFPM). The HPEM produces species densities and source

functions in the bulk plasma, and the trajectories of ions and neutral species onto the substrate. The MCFPM uses these fluxes and trajectories to evolve a deposition profile while considering energy and angular dependent deposition and sputtering probabilities. A surface diffusion algorithm was developed to avoid artificial dendritic growth. Cu deposition will be discussed for an inductively coupled plasma using a dc magnetron target. Typical operating conditions are 10's mTorr Ar buffer gas, 100's to 1000's kW ICP and magnetron power, and 10's V substrate bias. For constant ICP power, conformality improved and the likelihood of keyholes decreased as magnetron power decreased due to an increase in the ion-toneutral ratio in the reactant fluxes. Micro-voids are sometimes produced for these otherwise "good" conditions due to microtrenching which occurs by ion-reflection neutrals during resputtering of the deposited metal. Similar effects are seen by increasing buffer gas pressure to increase ionization fraction. The consequences of surface diffusion on the profile will also be examined. @FootnoteText@ @footnote 1@Work supported by TAZ, Novellus, AMAT, SRC and NSF.

# 4:20pm **PS2-WeA8 Process Characterization for Tapered Contact Etch**, *F.G. Celii, Q. He, J. DeBord*, Texas Instruments, Inc.; *H. Sakima*, Tokyo Electron America

The demands placed on lithography by the constant reduction in feature size can sometimes be alleviated in conjunction with the etch process. For line patterning, photoresist trimming gives a large etch bias and reduces linewidths well-below the lithography limit. For hole patterning, a tapered etch profile results in a bottom hole diameter which can be significantly smaller than the patterned CD. We report the characterization of contact etch processes which give variable sidewall taper angles. Patterning at 248 nm gave contact holes at ~0.19  $\mu m$  diameter in photoresist over organic BARC. The contact stack (BARC/oxide/SiN, 6 - 10 kÅ total stack thickness) was etched in a medium-density TEL Dipole Ring Magnetron (DRM) system. Bottom hole diameters ranging from 0.17 µm down to 0.10 µm could be obtained by varying the oxide etch process, which included C@sub 4@F@sub 8@ or C@sub 5@F@sub 8@, O@sub 2@ and Ar. Moderate etch selectivity to SiN (>10:1) was needed because of the bi-level contact height (over gate or over active). Etched patterned wafers were characterized using top-down CD-SEM, cross-section SEM and TEM. Ex situ surface analysis of etched blanket wafers was made to test the model of fluorocarbon film control of etch selectivity. Electrical properties of the Wfilled contacts will also be summarized.

# 4:40pm PS2-WeA9 Understanding the Evolution of Trench Profiles in the Via-First Dual Damascene Integration Scheme, *T. Kropewnicki, K. Doan, B. Tang, C. Björkman,* Applied Materials

Many surprising shapes of via profiles and trench bottoms have been observed during trench etch of the via-first dual damascene integration scheme. The most common features are faceting of the existing via holes as the trench etch progresses and fencing around the via holes. These particular features can lead to problems during copper metallization and ultimately to device failure. Therefore, it is imperative that the evolution of these features be understood so that they can be avoided. This paper will present experimental results indicating that the evolution of these features is heavily dependent upon the existing via profile and whether bottom antireflection coating (BARC) or photoresist (PR) is in the via hole prior to starting the trench etch. The proposed mechanism for faceting of the via hole is preferential sputtering of the top edge of the via. Fencing results when BARC or PR on the via sidewall vertically mask the underlying oxide when the via wall is sloped. Our empirical model for fence and facet formation was confirmed by a simple profile simulator. Finally, several options for avoiding the evolution of fencing and faceting during the trench etch will be proposed.

# 5:00pm PS2-WeA10 Microtrenching, Etching and Sidewall Passivation in Contact Holes and Edge Regions, *B. Abraham-Shrauner, C. Liu,* Washington University

Our analytical/numerical models for etching in semiconductor fabrication of integrated circuits are extended to include sidewall passivation and microtreching for contact holes (vias) and edge regions. The models fit oxide etch profiles in SEMS in a CF4/CHF3/Ar plasma.@footnote 1@ Neither grazing scattering of ions from the feature sidewalls@footnote 2@ nor the deviation of the ion trajectories by sidewall charging@footnote 3@ are needed to model mild microtrenching. The model for contact holes includes a new approximate analytic expression for the ion energy flux, Langmuir kinetics for the ions and etching neutrals and the flux for deposition neutrals. The deposition neutrals are modeled by an interpolation between shadowed and isotropic neutrals. The edge region

(half trench) model may include enhanced microtreching by scattered ions or distortion of ion trajectories by sidewall charging. The basic shape of the etch profile of the half trench is determined by the ion energy flux and the deposition flux and most of the sidewall is a characteristic of the evolution PDE. @FootnoteText@ @footnote 1@ Etch profile data was furnished by M. J. Buie and J. T. P. Pender of Applied Materials. @footnote 2@ M. Schaepkens and G. S. Oehrlein, Applied Phys. Lett. 72, 1293(1998). @footnote 3@ T. J. Dalton, J. C. Arnold, H. H. Sawin, S. Swan, D. Corliss, J. Electrochem. Soc. 140, 2395 (1993).

### Plasma Science and Technology Room 310 - Session PS1+TF+SE-ThM

## Fundamentals of Plasma Enhanced Chemical Vapor Deposition

Moderator: A. von Keudell, Max-Planck-Institut für Plasmaphysik

8:20am PS1+TF+SE-ThM1 Analysis of Pulsed O@sub 2@/TEOS Helicon Plasmas by Time-resolved Optical Spectroscopy, *A. Granier*, Institut des Materiaux de Nantes, France; *A. Rousseau*, Laboratoire de Physique des Gaz et des Plasmas, France; *L. Le Brizoual*, Institut des Materiaux de Nantes, France

The use of pulsed plasmas instead of continuous plasmas in Plasma Enhanced Chemical Vapor Deposition is known to improve film quality and adherence, due to the reduction of stress. Here, pulsed low pressure (2 mTorr) helicon oxygen/tetraethoxysilane (TEOS) plasmas are investigated by time-resolved optical emission spectroscopy in order to monitor the kinetics and lifetime of radical species in the plasma-off and plasma-on periods. The 300W rf power is 100% modulated and the duty cycle is varied from 1 to 500 Hz. The time behavior of Ar (750 nm), O (844 nm), H (486 nm), OH (306 nm) and CO (296 nm) emissions in the diffusion chamber are studied. The Ar line takes less than 100 microseconds to reach its equilibrium. The H. OH. O and CO intensities take significantly greater times to equilibrate due to the relatively long lifetime of their ground states, and it was necessary to go to a duty cycle of 1 Hz, including a 130 ms plasma-on time and a 860 ms plasma-off time to reach the stationary state. Under the plasma conditions investigated (a 2 mTorr pressure including a TEOS partial pressure of 0.2 mTorr) the OH, O, H intensities take about 1ms, 40ms and 80 ms, respectively to reach their equilibrium. In addition, their intensities normalized to the Argon line intensity increase from a value close to zero at the ignition time, which indicates that the excited states of OH, O, H radicals are created by electron impact excitation on their ground-states and that these radicals have completely disappeared after 860 ms. In contrast, the normalized CO intensity increases from almost zero but has not yet reached its equilibrium after 130 ms, which is consistent with the fact that CO is a stable molecule which is lost by convection to the pump. Additional results obtained in pure oxygen plasmas are also presented and compared to those obtained in O@sub 2@/TEOS plasma.

#### 8:40am PS1+TF+SE-ThM2 Aluminum Oxide Deposition in an Ionized PVD System, N. L<sup>1</sup>, D.N. Ruzic, University of Illinios, Urbana-Champaign; A. Paranjpe, CVC Inc.; J.E. Norman, J.P. Allain, University of Illinios, Urbana-Champaign

An Aluminum target of a planar magnetron system is powered by a pulsed DC plasma generator to deposit AlOx film using a mixture of Ar and O2. Compared with the conventional sputtering magnetron system, the pulsed directed current (DC) bias is able to discharge the accumulated ions on the insulating AlOx film surface effectively during the positive duty cycle. The chamber also contains a secondary radio-frequency (RF) plasma source to ionize the sputtered metal neutral flux, and generate oxygen atoms and radicals. The directionality of the ion flux can be important for high aspect ratio features. The deposition rates of AI and AIOx films as a function of O2 partial pressure vs. Ar are examined with and without the RF plasma. The deposition rate of AlOx with 400 Watts RF is actually much higher than the deposition rate of Al without the RF at the same total pressure of 25mTorr. Hysterisis curves showing the transition point from metallic mode to poison mode at a certain partial pressure are presented. The presence of a secondary plasma producing ionization makes the metallic sputtering mode possible at a higher O2 partial pressure. A gridded energy analyzer and a guartz crystal microbalance (QCM) are embedded in the substrate plane to allow the ion and neutral deposition rates to be determined. Electron density and electron temperature changes caused by the RF power are measured by a Langmuir Probe. SEM photos of deposited films show differences in film quality as a function of RF power.

#### 9:00am PS1+TF+SE-ThM3 Surface Transport Kinetics in Plasma Deposition of Hydrogenated Amorphous Silicon, K.R. Bray, A. Gupta, G.N. Parsons, North Carolina State University

The concept of dynamic scaling was developed to help understand the role of kinetic phenomena that occur on surfaces during non-equilibrium processes (such as film deposition). Plasma deposition of a-Si:H is particularly intriguing because it is well known that over a wide

temperature range, kinetic growth process results in very smooth (nonrandom) surface texture indicating significant surface species transport, but the growth rate is not thermally activated. We have used rf plasma deposition to form a-Si:H films with both helium and argon diluted silane, and used dimensional and frequency analyses to analyze surface topography obtained from AFM images. Surface fractal scaling parameters, including static (a) and dynamic (b) scaling coefficients, Fourier index, saturation roughness, and lateral correlation length (Lc), were determined as a function of film thickness and temperature. After film coalescence (15-20 s) the scaling coefficients are consistent with the surface topology being described as a self-similar structure; a is constant with growth time and is ~1.0, b is ~4.0, and the saturation roughness value increases exponentially with time as tb/a. Based on Herring's models of surface transport, the scaling coefficient values are consistent with surface smoothening being driven by diffusion. In this picture, the lateral correlation length can be equated with the surface diffusion length. We find that Lc ranges from ~50 to 200nm, and is thermally activated, corresponding to a diffusion activation energy of ~0.2eV. This result has important implications for current growth models, where diffusion length is proposed to decrease with increasing temperature because of increasing density of diffusionterminating dangling bond sites. Possible modifications to current models, consistent with our observed data, will be discussed and presented.

9:20am **PS1+TF+SE-ThM4 Hydrogenated Amorphous Silicon Fractal Growth and its Relation to the Growth Mechanism**, *A.H.M. Smets*, Eindhoven University of Technology, The Netherlands; *D.C. Schram*, Eindhoven University of Technology, The Netherlands, Netherlands; *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

The roughness evolution of the anorphous hydrogenated amorphous silicon (a-Si:H) growth has been studied using in situ HeNe ellipsometry. The a-Si:H depositions are performed using expanding thermal plasma (ETP) deposition technique. With the ETP technique it is possible to grow a-Si:H under dominantly SiH@sub 3@ flux conditions with growth rates ranging over two orders magnitude (1-100 Å/s). The roughness evolution can be divided in an initial growth phase corresponding to a nucleation phase followed by a post initial phase in which the a-Si: H bulk is grown. The post initial growth phase can be described following the universal scaling law, i.e. the roughness scales as t@super beta@ where t is the time and @beta@ the dynamic scaling exponent which depends on the surface relaxation mechanism. The measured scaling exponent @beta@ for growth rates equal or smaller than 22 Å/s is temperature dependent and drops from 0.5 at 100 Celsius down to 0.06 at 500 Celsius. A simple solid on solid (SOS) model is introduced, based upon an activated site at which growth can occur and which can diffuse with a site dependent surface diffusion. With this model the temperature dependent @beta@ can be simulated and the activation energy of the diffusion mechanism can be deduced without the knowledge which process is really responsible for the surface relaxation. The obtained activation energy is equal to ~ 1.0 eV on a terrace site, much higher then what would be expected from physisorbed SiH@sub 3@ dominated a-Si:H growth. At higher growth rates (70 Å/s) the @beta@ shows a maximum around 300 C Celsius. The obtained @beta@ at low temperatures and high deposition rates corresponds to a phase in which the roughness evolution tends more to ballistic fractal growth. Possible relaxation mechanism to explain the high diffusion activation energy will be discussed.

9:40am PS1+TF+SE-ThM5 Interactions of Chemically Reactive Radicals with Si Growth Surfaces during Plasma Deposition of Si Thin Films, S. Sriraman, University of California, Santa Barbara, U.S.A; S. Ramalingam, E.S. Aydil, D. Maroudas, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. The structural quality and electronic properties of the deposited films depend on the identities and fluxes of chemically reactive species that originate in the plasma and impinge on the growth surface. Atomic-scale simulations of radical-surface interactions are of utmost importance in understanding the fundamental mechanisms of the deposition process. In this presentation, moleculardynamics (MD) simulations of radical-surface interactions during deposition of a-Si:H from chemically reactive radicals, SiH and SiH@sub 2@, are analyzed. The simulations reveal a broad class of reaction mechanisms and predict surface reaction probabilities that are in good agreement with experimental measurements. The growth of a-Si:H films starting from an initial H-terminated dimerized Si(001) surface is studied through MD simulations of repeated impingement of the individual radical precursors. Special emphasis is placed on the identification of the

elementary surface chemical reactions that govern the deposition process. Effects of the reactions on the growth surface are examined by analyzing local structural configurations and surface chemical reactivity in the vicinity of the surface reaction sites. Evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition are analyzed in detail and comparisons made with similar films deposited from individual SiH@sub 3@ precursor. The resulting surface hydride compositions in the deposited films are compared with experimental data. The comparisons are used to discuss our current understanding of the deposition process and implications for plasma deposition of a-Si:H.

# 10:00am PS1+TF+SE-ThM6 SiH@sub x@ Radical Densities in a Remote SiH@sub 4@ Plasma for High Rate Deposition of a-Si:H, W.M.M. Kessels,

J.P.M. Hoefnagels, M.G.H. Boogaarts, Eindhoven University of Technology, The Netherlands; D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

The ground state densities of SiH@sub x@ radicals in a remote Ar-H@sub 2@-SiH@sub 4@ plasma used for high rate deposition of device quality a-Si:H (up to 100 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CDRS) and threshold ionization mass spectrometry (TIMS). SiH@sub 3@ has been measured by CRDS using the broadband à @super 2@A@sub 1@ <- @td X@ @super 2@A@sub 1@ absorption peak at 200 - 260 nm and revealed very good agreement with the TIMS measurements on SiH@sub 3@. SiH@sub 2@ has been measured by TIMS and SiH and Si by CRDS on the transitions A @super 2@@DELTA@ <- X @super 2@@PI@ (~414 nm) and 3p4s <- 3p@super 2@ (~251 nm), respectively. The generation and loss processes for the silane radicals have been investigated thoroughly for different plasma conditions and the contribution of the radicals to film growth has been determined. It is shown that for optimum a-Si:H film properties, the contribution of SiH@sub 3@ is approximately 90%, of SiH@sub 2@ is smaller than 5%, of SiH is ~2%, and of Si is 0.2%. For these conditions, the spatially resolved axial and radial SiH@sub 3@ densities in the plasma are compared with 2-D axisymmetric fluid dynamics model calculations using Phoenics CVD, in which the basic gas phase and surface reactions are taken into account. Furthermore, the first time-resolved silane radical measurements in a modulated rf biased plasma for the determination of the radicals' surface reaction probability will be presented.

# 10:20am PS1+TF+SE-ThM7 Fundamentals of Plasma Enhanced Chemical Vapor Deposition, J. Meichsner, Ernst-Moritz-Arndt-University Greifswald, Germany INVITED

Applications of non-isothermal plasmas for chemical vapor deposition and plasma surface modification imply the understanding of the fundamental problem: the plasma-surface interaction. From the plasma physics point of view the transition between the gas plasma and the solid state is characterized by the plasma sheath in front of the surface which controls the flux and kinetic energy of the charged particles. Additionally, in a reactive molecular plasma the complex chemical reactions must be taken into account in the gas phase and at surfaces. Depending on nature of molecular gases, surface material and plasma properties the modification of a thin surface layer, etching or thin film deposition may be found simultaneously on electrodes, immersed samples or surrounding walls. Insitu diagnostic tools are preferably qualified to provide detailed information about processes in the gas plasma and at surfaces. The experimental investigations involved plasma diagnostics by means of optical spectroscopy (OES, LIF) and mass spectrometry (energy selective ion analysis, electron attachment mass spectrometry) as well as surface and thin film characterization using special methods of FTIR-spectroscopy (IRRAS, ATR, fiber based), ellipsometry and microgravimetry. In a low pressure rf-discharge of Hexamethyldisiloxane the chemical conversion of the monomer gas into new stable gas molecules and deposition of a thin organic film were investigated in dependence on characteristic process parameters. The changed atomic composition and molecular structure of the organic films were connected with varied film properties interesting for semipermeable membranes, photo-conducting films, optical or protective coatings. In fluorocarbon plasmas the investigation of the Polyethylene and Polystyrene surface modification as well as thin film deposition revealed the dynamics between incorporation of atoms/molecules and etching of surface material.

11:00am PS1+TF+SE-ThM9 Thin Film Growth via Surface Reactions of CH@sub 3@, C@sub 2@H@sub 2@ and H as Investigated by Radical Beam Experiments, *M. Meier*<sup>1</sup>, *A. von Keudell*, Max-Planck-Institut für Plasmaphysik, Germany

The knowledge about surface reactions of hydrocarbon radicals is a key element for the understanding of thin film growth in low temperature plasmas using hydrocarbons as precursor gas. Besides the formation of hard coatings by using an additional ion bombardment during growth, it is possible to deposit polycrystalline diamond at elevated substrate temperature from a methane discharge diluted in 99 % hydrogen. The dominant species which are believed to be responsible for diamond formation are atomic hydrogen together with either CH@sub 3@ or C@sub 2@H@sub 2@. In our experiment, we employ particle sources for the production of quantified beams of the radicals CH@sub 3@ and H and for C@sub 2@H@sub 2@ molecules to study the interaction of these species with a hydrocarbon film surface. The emitted fluxes of these beam sources are quantified by using angular resolved ionization threshold mass spectrometry. Recently it has been shown that the sticking coefficient of CH@sub 3@ increases from 10@super -4@ to 10@super -2@ if atomic hydrogen reacts simultaneously with the growing film surface at a low substrate temperature of 320 K. A similar experiment using C@sub 2@H@sub 2@ and H revealed no significant growth via C@sub 2@H@sub 2@ adsorption at the film surface. The variation in the film composition during the synergistic growth is monitored via in situ real time infrared spectroscopy. From the interpretation of these spectra a growth synergism for the simultaneous interaction of CH@sub 3@ and C@sub 2@H radicals with the film surface is observed. This demonstrates that the various synergisms between the growth precursors have to be taken into account for a consistent description of thin film growth via radical adsorption.

# 11:20am PS1+TF+SE-ThM10 Deposition Kinetics in Methane rf Glow Discharges: A Combined Experimental and Modeling Study, J.R. Doyle, D. Cole, B. Magocsi, Macalester College

Methane rf glow discharges are commonly used for diamond-like carbon deposition, but in spite of many experimental and theoretical studies, the details of the plasma chemistry, and in particular the identity of the dominant film precursors, are still debated. In this work we present a comprehensive model of the film deposition using a "semi-empirical" approach. Optical emission measurements and measured electrical properties of the discharge are combined with a Particle-in-Cell/Monte Carlo (PICMC) simulation, which is then used to calculate ion and neutral radical production rates and profiles. Diffusion-reaction-drift (fluid) equations are then solved for stable gas production and ion and radical transport to the electrode surfaces. The model is corroborated by mass spectrometry measurements of the stable gas partial pressures. Film growth rates are calculated from the model and are compared to measured growth rates as a function of pressure and power on both the grounded and powered electrode. The results suggest that C@sub n@H@sub m@ radicals and ions with n > 1 are the dominant sources of mass deposition under conditions used to produce diamond-like films.

# 11:40am PS1+TF+SE-ThM11 Using Plasma Energetics to Influence Silicon Nitride Step Coverage, K.L. Seaward, Agilent Technologies; M.L. Jezl, University of Wisconsin, Madison

PECVD silicon nitride is widely used in the fabrication of electronic and optical devices, integrated circuits, and display devices. An important characteristic of PECVD silicon nitride is step coverage, which describes how well the deposition conforms to features that are being coated. Both high and low step coverage are technologically important. In the present work, we investigate altering the plasma energetics to change the amount of PECVD silicon nitride deposited on the underside of structures. Models that predict such step coverage suggest that the precursor sticking coefficient is the dominant factor. Accordingly, different inert gases were added to the deposition plasma to either increase or decrease sticking coefficients by way of increasing or decreasing the plasma electron energy. Depositions were run with 4% ammonia, 1% silane, and 95% He, Ar, Xe, or N@sub 2@. Deposited films were characterized by etch rate, stress, FTIR, Auger, and SEM. Deposition plasmas were characterized by optical emission and rf tuning parameters. The only characteristic related to step coverage was the ratio of N-H bonds to Si-H bonds in the films. Since PECVD silicon nitride films have between 10% and 30% hydrogen content, it is expected that hydrogen plays a large role in film properties. What appears to happen for step coverage is a change in bonding configuration from nitrogen being primarily three-fold coordinated to silicon (high step

<sup>1</sup> PSTD Coburn-Winters Student Award Finalist

coverage) to nitrogen being primarily two-fold coordinated to silicon with the third bond being to hydrogen (low step coverage). This latter material, called silicon diimide, is a chemical analog of SiO@sub2@ which, when plasma-deposited with silane, also has low step coverage. This analogy with SiO@sub2@ deposition suggests that precursor sticking coefficients are high during formation of silicon diimide, and this occurred most prominently with mixtures of He and N@sub2@ present in the plasma.

### Plasma Science and Technology Room 311 - Session PS2-ThM

#### **Plasma Diagnostics II**

Moderator: E.A. Edelberg, Lam Research Corporation

8:20am PS2-ThM1 Advanced Actinometry of Inductively Coupled Cl@sub 2@-Ar Plasmas For Plasma Etching, N.C.M. Fuller, I.P. Herman, Columbia University; V.M. Donnelly, Bell Laboratories, Lucent Technologies

The exact composition of Cl@sub 2@-Ar plasmas can influence the overall mechanism and rates of adlayer formation and removal (ion-induced sputtering) during the etching of various materials; therefore, the mixture composition can be altered to improve the overall plasma chemical etching process. To this end, optical emission spectroscopy (OES) and Langmuir probe analysis have been used to measure the electron temperature, T@sub e@ and the absolute species densities in a high-density inductively coupled (ICP) chlorine-argon plasma at 18 mTorr as function of the 13.56 MHz radio frequency (rf) power and argon fraction. In the H (bright) mode, the electron temperature. T@sub e@, measured by trace rare gases optical emission spectroscopy (TRG-OES), increases from 3 eV at 350 W to ~ 6 eV at 770 W for a chlorine plasma (1% Ar). At 600 W (10.6 Wcm@super -2@), T@sub e@ increases from 5.0 eV to ~ 6.5 eV as the argon fraction increases from 0.01 to 0.73. In the E mode at 200 W, the fraction of Cl@sub 2@ that dissociates to form Cl increases from ~10% to ~ 40% as the argon fraction increases from 0.01 to 0.73. In the H mode at 600 W, this dissociation fraction increases from 82% to 96% over the same range. In the H mode and for all argon fractions, the electron density, calculated by a global model, increases by at least an order of magnitude from 300 W to ~ 750 W, and at 600 W it decreases from 1.0 x 10@super 12@ cm@super -3@ to 5.5 x 10@super 10@ cm@super -3@ as the argon fraction increases from 0.01 to 0.73. OES is also used to estimate the peak value of the electron impact excitation cross section for the dissociative excitation of Cl@sub 2@ to the Cl (4p@super 2@ D@super 0@ J@super '@ = 3/2, 5/2) excited state with subsequent emission at 822.2 nm. This peak value is 1.7±0.3 x 10@super -19@ cm@super 2@. The changes in the surface adlayer when the mixture composition is varied will also be discussed.

#### 8:40am PS2-ThM2 Diagnostics of Inductively Coupled Chlorine Plasmas: Measurements of the Neutral Gas Temperature, V.M. Donnelly, M.V. Malyshev, Bell Laboratories, Lucent Technologies

We report measurements of the bulk, neutral gas temperature in a chlorine inductively coupled (ICP), or transformer-coupled plasma (TCP). A trace amount (2-5%) of N@sub 2@ was added to the discharge and the rotational temperature of the C-state was determined from the C->B emission in the ultraviolet. This temperature has been shown by others to be equal the rotational temperature of ground state N@sub 2@, which is the thermally equilibrated (translational and rotational) gas temperature (T@sub g@). The gas temperature 3 cm above the wafer is equal to, or only slightly above the wall temperature (300 K) throughout the low-power, capacitively-coupled regime (

#### 9:00am PS2-ThM3 A New Diagnostic Method for Monitoring Plasma Reactor Walls: Multiple Total Internal Reflection Infrared Surface Probe, *A.R. Godfrey, S.J. Ullal, E.S. Aydil,* University of California, Santa Barbara; *E.A. Edelberg, L.B. Braly, V. Vahedi,* Lam Research Corporation

One of the major concerns in plasma etching of thin films with high density inductively coupled plasma (ICP) reactors is wafer-to-wafer etch rate reproducibility. Inductively coupled plasma reactors are typically operated at low pressures where the mean free path of species in the plasma is on the order of the reactor dimensions. As a result, reactive radicals collide with the chamber walls as often as they do with each other in the gas phase and the walls play a crucial role in determining the plasma properties and etching behavior. Thus, it is critical to monitor the wall conditions and the nature of the films and adsorbates that are deposited on the walls. We have developed a surface probe based on in situ multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy that can be used as a diagnostic technique to monitor the films and adsorbates on the

walls of both plasma etching and deposition reactors. A small (5 cm x 1 cm x 0.1 cm) trapezoidal shaped infrared transparent crystal with 45° beveled edges is placed flush with the reactor walls with the beveled edges facing small IR transparent windows. Infrared beam from a spectrometer is focused onto one of the beveled edges and made to undergo multiple total internal reflection through the crystal before exiting it from the opposite beveled edge. The films deposited on the crystal surface are sampled by the infrared beam which is collected and detected using an IR detector. This diagnostic method enables in situ monitoring of the deposits on the reactor walls during plasma processing. The MTIR-FTIR surface probe and its applications to monitoring reactor walls during plasma etching and deposition processes will be described in detail. Specifically, this talk with emphasize application of the MTIR-FTIR probe to monitoring the walls of a Lam ICP reactor during etching of Si with Cl@sub 2@/O@sub 2@ gases and subsequent cleaning in between etched wafers with a F containing discharge.

#### 9:20am PS2-ThM4 Laser-Aided Diagnostics of Discharge Plasmas, K. Muraoka, K. Uchino, M. Bowden, M. Maeda, Kyushu University, Japan INVITED

In order to understand, and ultimately optimize discharge plasmas for various purposes, we have to know spatio-temporal distributions of (1) electric fields, (2) electron density and temperature (or EEDF itself if it is away from Maxwellian), and (3) reaction products. The authors have extensively explored potentials of laser-aided plasma diagnostics (LAPD) for this purpose and applied it to various discharges. These are developments and applications of laser optogalvanic spectroscopy (LOG) and laser-induced fluorescence (LIF) to detect Stark effect for (1), Thomson scattering to measure electron density and temperature/EEDF for (2), and LIF, Raman scattering, Rayleigh scattering, and ultra-violet absorption to measure density and temperature of atoms and molecules for (3). Each of these is described, with a special emphasis being placed on (2).

### 10:00am PS2-ThM6 Energy Distributions of Incident Ions to a RF-Biased Substratep, H. Kawada, N. Tsumaki, Hitachi Ltd., Japan

Energy distributions of incident ions and molecules to a substrate exposed to a plasma generated in fluorocarbon gas was obtained by a Quadrupole Mass Spectrometer equipped with an energy filter which was operated with time modulation. The incident ions a nd molecules which entered into an orifice opened in the substrate surface were analyzed by the QMS mounted under the orifice. An 800-kHz radio frequency (rf) voltage was applied to the substrate, as it is commonly done in order to enhance dry etching rea ction on wafers mounted on the substrate. Because of the alternating voltage in the rf, an electrical potential of the substrate is also alternating and not constant. On the other hand, the reference potential used for the QMS optics is not always equal t o the potential of the substrate because the QMS optics must be electrically insulated and kept stable for normal operation. Therefore, post-acceleration of the ions would occur by the unstable potential difference between the substrate and the QMS optics, after the incident ions has received kinetic energy in acceleration between the plasma and the substrate. Such the postacceleration causes a large error in measuring the kinetic energy that is essential of the incident energy. In order to obtain real energy distributions by minimizing the post-acceleration, time modulation was carried out in our detection setup, that is, the incident energy was measured only at the moment when the rf voltage of the substrate was equal to the reference potential in the QMS optics. Furthermore, by varying the reference potential, the incident energy could be measured at a specific phase of the rf voltage of the substrate. We also measured relative densities of radicals caused in the plasma by using Infrared Laser Absorption Spectroscopy. The energy distributions of the incident ions at a specific bias phase, and its correlation to the radical densities will be shown and discussed.

#### 10:20am **PS2-ThM7 Energy and Angular Distribution of Ions Effusing from a Hole in Contact with a High Density Plasma**, **D. Kim**, C.-K. Kim, D.J. Economou, University of Houston

The energy and angular distribution of ions extracted from a hole in contact with a low- temperature plasma have been investigated both computationally and experimentally. A single hole is thought to be a well-defined system for understanding the interaction of a plasma with a biased grid. Such plasma-grid interaction finds applications in neutral beam etching, ion sources, satellite thrusters, etc. The plasma parameters (Debye length), hole diameter and thickness determine the characteristics of the ions (and fast neutrals) extracted through the hole. We have developed a Monte Carlo simulation to follow the trajectories of ions and fast neutrals from the bulk plasma through the sheath and out the hole. Collisions with

gas phase species and the walls of the hole are taken into account. We have also measured the energy and angular distribution of ions effusing from a hole on a wall in contact with a high density plasma. A hemispherical sectioned electrode is used as the detector. The hole diameter is varied from 25 to 1000 microns and the hole aspect ratio (depth to diameter) is varied from 0.25 to 10. The energy and angular distributions in both experimental data and simulations reflect the strong disturbance of the sheath when the hole size exceeds the local Debye length.

# 10:40am PS2-ThM8 Electron Temperature and Ion Energy Measurements with A High-resolution, Sub-micron, Retarding Field Analyzer, *M.J. Sowa, M.G. Blain, R.L. Jarecki, J.E. Stevens,* Sandia National Laboratories

A silicon wafer-based, submicron, high-resolution, retarding field analyzer (RFA)@footnote 1@ was used to measure ion energy and infer electron temperature (Te) in an inductively coupled plasma. RFA ion energy measurements are expected to have a resolution of < 0.1 eV based on simulations. By monitoring the flux of ions to the collector of the RFA while allowing the shield to float, we are able to measure the local difference between the plasma and floating potentials. From this difference, the electron temperature can be calculated directly from sheath theory. Experimental conditions include 10, 20, and 40 mTorr Ar at 100, 200, and 300 W of plasma source power at axial positions of 42-217 mm from the source dielectric window. RFA Te values were compared to those obtained with single and double probes. Excellent agreement was observed between the single probe and RFA over all conditions. Double probe measurements matched the other measurement techniques at 20 and 40 mTorr, and gave 5-30% higher Te values at 10 mTorr. The ion energy spreads measured with the RFA are close to Gaussian with standard deviations from 1.8-2.2 eV. The ion energy spread increased weakly with pressure but showed little dependence on the position or the measured Te value, which ranged from 1.3 - 2.7 eV.@footnote 2@ @FootnoteText@ @footnote 1@ M.G. Blain, J.E. Stevens, J.R. Woodworth, Appl. Phys. Lett., v.75, n.25, p.3923, 1999. @footnote 2@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

#### 11:00am PS2-ThM9 Mass Resolved Ion Energy Distribution Measurements in an Inductively Coupled H@sub 2@/Ar Plasma with a Highly Collisional Presheath, S. Agarwal, D. Maroudas, E.S. Aydil, University of California, Santa Barbara

Ion energy distributions (IEDs) in a plasma are determined by the spatiotemporal variation of the potential in the sheath and the presheath. In practice, it is not possible to directly measure the electric field in these regions as they are very thin and easily perturbed by a probe. However, in cases were the preseheath/sheath is collisional and/or the transit time through the sheath is comparable to the rf cycle, structured ion energy distributions are obtained which may be used to compute the electric field in the plasma near a surface. Mass-resolved IED measurements were made using a QMS equipped with a Bessel box energy analyzer in a H2/Ar plasma. The ions were sampled through an aperture on the grounded electrode in a helical resonator plasma reactor through a 2.8 degrees solid angle to detect mostly those ions that have been created by inelastic collisions. These ions preserve information about the electric fields in the sheath and the presheath. The ionic species detected were H+, H2+, H3+, Ar+, and ArH+. The IEDs for H+, H2+ and H3+ showed multiple peaks (as many as 20) superimposed on a saddle structure whereas the IEDs for Ar+ and ArH+ showed only a single peak approximately centered at the time averaged plasma potential. The saddle shaped IED arises because the transit time through the sheath for the lighter ions is less than the rf cycle and the multiple peaks arise due to charge exchange or proton transfer reactions or electron impact ionization in the quasi-neutral presheath region. If there are collisions in the sheath, the peaks appear at an energy lower than the saddle shaped curve. However, in the present measurements, the peaks were superimposed on the saddle curve itself, which means that they arise from collisions in the presheath and subsequent splitting of this multi-peaked distribution in the thin collisionless sheath region. The number and position of the peaks can be used in principle to reconstruct the electric field in the plasma.

#### 11:20am **PS2-ThM10 Langmuir Probe Analysis for High Density Plasmas**, *F.F. Chen*, University of California, Los Angeles

The theory of Langmuir probes has been reexamined for use in high-density plasma tools with plasmas in the N = 10@super 11-13@ cm@super -3@ range. The most accurate computations for collisionless plasmas have been done by Laframboise,@footnote 1@ but the results are difficult to

apply to data because of the normalized units used. Up to now, for densities in the 10@super 9-11@ cm@-3@ range, the simpler Orbital Motion Limited (OML) theory has sufficed. The two theories agree at low densities. To make the Laframboise curves accessible for real-time I - V analysis of probe data at higher N, we have found analytic approximations to the curves by a double parametrization technique. Furthermore, an iterative procedure permits separating the ion and electron currents in their overlap region, thus yielding an accurate fit to the shape of the ion characteristic and hence accurate values of N and KT@sub e@ regardless of the density range. Comparison with experiment, however, gives surprising results. For N such that the ratio of probe radius to Debye length exceeds 3 (thin sheaths), the OML theory is expected to fail, but it fits the SHAPE of the ion characteristics better than the Laframboise theory, which gives N values 2-3 times higher. The latter seems to agree better with independent measurements of N using microwaves or plasma oscillation probes. We have also parametrized an intermediate theory, that of Allen, Boyd, and Reynolds,@footnote 2@ but this gives unreasonably low N values. A possible cause of the paradox is the effect of charge-exchange collisions. @FootnoteText@ @Footnote 1@ Laframboise, J.G., Univ. Toronto Inst. Aerospace Studies Rept. 100 (June, 1966). @Footnote 2@ Allen, J.E., Boyd, R.L.F., and Reynolds, P., Proc. Phys. Soc. (London) B70, 297 (1957).

11:40am PS2-ThM11 Single Photon Ionization as a Probe of Radicals in Hot-Wire and Plasma Processing, H.L. Duan, S.F. Bent, Stanford University Gas phase radicals produced in both plasma and hot-wire sources for etching or deposition can influence reaction pathways, reaction rates, and product distributions. Identifying and monitoring the concentrations of free radicals during processing is generally difficult due to the short radical lifetime and low radical concentrations relative to the background. Here we describe the use of a single-photon vacuum ultraviolet (VUV) photoionization technique for the detection of free radicals during thin film growth. In this technique, VUV radiation at 118 nm is generated by frequency mixing of the output of a pulsed Nd:YAG laser to obtain the ninth harmonic. Photons at 10.5 eV contain sufficient energy to ionize many radicals of interest; the laser-ionized ra dicals are then detected by time of flight mass spectrometry. The potential of SPI as a radical probe in electronic materials processing will be demonstrated in studies of two chemical vapor deposition systems using hot-wire activation (HW-CVD): growth o f amorphous hydrogenated silicon (a-Si:H) thin films using silane and growth of amorphous silicon carbon alloys from methylsilane precursor gases. The SPI probe allows for simultaneous detection of Si, SiH@sub x@, Si@sub 2@H@sub y@, and CH@sub 3@ radicals present in the gas phase. It is shown that, other than H atoms, Si atoms are the dominant radicals produced by the hot tungsten filament in the presence of silane. Hydrogen dilution is found to change the gas phase silyl radical distribution. In the case of methylsilane decomposition on the hot wire, methyl radicals are produced in addition to Si-containing radicals. Studies as a function of filament temperature, filament aging, and hydrogen dilution demonstrate the strength of this technique for monitoring reactive radicals in situ with both spatial and temporal resolution. The use of the SPI method for radical detection in plasma processing will also be discussed.

### Plasma Science and Technology Room 310 - Session PS1-ThA

**Plasma-Surface Interactions II** 

Moderator: C.B. Labelle, Bell Laboratories, Lucent Technologies

2:00pm **PS1-ThA1 Plasma Surface Modification of PET and Acrylic Coating Surfaces**, *M.K. Shi*, Pacific Northwest National Laboratory, U.S.; *A. Tyryshkin*, Princeton University; *G.C. Dunham*, *M. Bowman*, *G.L. Graff*, *P.M. Martin*, *G.J. Exarhos*, Pacific Northwest National Laboratory

Plasma treatment has proven to be very effective in modifying polymer surface properties for enhanced surface compatibility and adhesion. The treatment is performed in vacuum and the effect can be achieved within a few seconds. These characteristics make plasma technology extremely appealing for the adhesion promotion of polymer-metal multilayer stacks that can be deposited inline and at high speed in a vacuum web-coater. The surface modification of poly(ethylene-terephthalate) (PET) and UV-cured tripropyleneglycol diacrylate films induced by remote N@sub2@ and Ar microwave (2.45 GHz) plasmas was investigated in order to better understand the plasma/surface interaction mechanisms. In-situ XPS analysis revealed that N@sub2@ and Ar plasma treatments led to removal, in entirety, of the initial oxygen-containing groups on the polymer surfaces. The removal of ester groups was much faster for the acrylic than for the PET, and the removal of ether groups was much faster than that of ester groups within the acrylic film. Electron parametric resonance (EPR) measurements indicated the presence of several types of free radicals. The concentration of these radicals was higher for N@sub2@ than for Ar plasma treatment and for the acrylic than for the PET film, which correlated well with the more pronounced surface modifications measured by XPS. Pulsed EPR measurements suggested that these radicals existed mainly in radical pairs and were distributed within 2000 Å from the top surface. The concentration of free radicals correlated well with the amount of N incorporated into the surface by N@sub2@ plasma treatment. These results strongly supported a free radical-dominated plasma/surface interaction mechanism and highlighted the important role of plasma UV emission. Water contact angle measurements indicated that the incorporated N atoms were responsible for the improved surface wettability.

#### 2:20pm PS1-ThA2 Exploring Chemical Mechanisms behind Hydrophilic Surface Modification of Polymeric Membranes by Low-temperature Plasma Treatment, *M.L. Steen*<sup>1</sup>, *E.R. Fisher*, Colorado State University

We recently developed a surface modification strategy that renders asymmetric polymeric membranes permanently hydrophilic.@footnote1@ This entails treating asymmetric membranes with a low-temperature plasma to obtain the desired change in wettability. This treatment is quite versatile as polysulfone, polyethersulfone, and polyethylene membranes are completely hydrophilic as a result of plasma treatment. XPS results indicate that the desired change in wettability observed for plasma-treated membranes is a result of implantation of new, more hydrophilic functional groups by plasma treatment; however, little is known about the chemistry occurring on a molecualr level during plasma modification. Hence, we recently began investigating the mechanisms behind hydrophilic modification of asymmetric polymeric membranes. We have determined the gas-phase composition as well as ion and electron densities with optical emission sepctroscopy (OES), Langmuir probe studies and mass spectrometry. We suspect OH radicals, detected in the OES spectrum, are likely the species predominantly responsible for hydrophilic modification of our porous materials. Therefore, we have studied plasma-generated OH radical/surface reactivites with porous polymeric membranes as the substrate of interest by the IRIS (Imaging of Radicals Interacting with Surfaces) method. This technique is uniquely suited to afford chemical information critical to elucidation of the mechanisms responsible for plasma modification of porous materials. We will report OH reactivites at several porous polymeric substrates including asymmetric polysulfone, polyethersulfone, and polyethylene membranes. We will also present correlations drawn from the aforementioned techniques, proposing the role of OH radicals and other plasma-generated species in plasma processing of porous materials. @FootnoteText@ @footnote 1@M. L. Steen, L. Hymas, E. D. Havey and E. R. Fisher, J. Memb. Sci., to be submitted.

2:40pm **PS1-ThA3 The Mechanisms of Anisotropy Control in Plasma Etching Processes, L. Vallier**, CNRS/LTM, France; G. Cunge, CEA/LETI, France; J. Foucher, D. Fuard, CNRS/LTM, France; R.L. Inglebert, O. Joubert, LTM/CNRS, France INVITED

Anisotropic plasma etching of microelectronic materials is achieved thanks to the bombardment of energetic ions, allowing the etch directionality to be achieved, and the formation of volatile etch products, through ionassisted chemical etching reactions. In this talk, we demonstrate that the anisotropy control of an etch process is obtained via the re-deposition of heavy non-volatile etch products on the feature sidewalls. Experiments have been conducted on a very powerful plasma etch system dedicated to advanced studies. It consists in a Decoupled Plasma Source (DPS) from Applied Materials modified to host in situ diagnostics such as UV-visible ellipsometry, mass spectrometry, fast injection Langmuir probe and X-ray photoelectron spectroscopy (XPS). Etch processes have been developed for silicon gates, low k polymers as intermetal dielectrics and Aluminum as metal for interconnect. Strong correlations have been observed between sidewall passivation layer formation (analyzed by XPS), profile control (through SEM inspection) and etch products analyses (using mass spectrometry analyses). For each material investigated, we have observed that the anisotropy control is only achieved if a passivation layer is formed on the feature sidewalls. At the same time, ion mass spectra clearly shows the presence of non-volatile species: heavy carbon chains for low k polymer etching, and silicon oxide and their derivatives for silicon etching. Mass spectrometric results also indicate that the number density of theses species is varying as the square root of ion energy (DC bias), suggesting that they are produced by the sputtering of the reactive layers formed at the bottom of the etched features. Finally, these experiments show that passivation layers can be designed by tuning the etch product formation. An example of sidewall passivation engineering for poly gate etching will be shown with the formation of a controlled notched profile.

### 3:20pm **PS1-ThA5 Pulsed Plasma Polymerisation of Acrylic Acid**, *S. Fraser*, *D.B. Haddow, R.D. Short*, University of Sheffield, UK

The synthesis of thin plasma polymer films from radio frequency sustained glow discharges of small organic compounds is well documented. Films containing a high degree of retention of the starting monomers original functionality and structure can be deposited using a low power plasma. These plasmas can be sustained by continuous wave (CW) or by pulsing a higher input power to achieve a lower average power. Although there is substantial literature on the use of pulsed plasmas there has not been any investigation made of the pulsed rf plasma environment of monomers containing C, H, O, or N. We describe the application of mass spectrometry and ion energy analysis to probe the pulsed plasma environment of acrylic acid. Analysis of the deposited films was carried out by XPS. The input power was fixed at 50W and the effect of plasma off time was investigated with respect to a fixed on time (eg 5ms/40ms=11% duty cycle). In terms of functional group retention the pulsed 50W plasma at a duty cycle of 11% is equivalent to a 3-3.5W CW plasma. It was shown that in the pulsed plasma the amount of intact acrylic acid was greatly reduced. There is no evidence in the pulsed plasma gas phase neutrals for significant radical-neutral or radical-radical combination. Any neutral species detected can be explained by homolytic cleavage of the carboxyl group and subsequent addition or loss of H. The positive ion mass spectrum of the pulsed acrylic acid plasma shows extensive gas phase oligomerisation was detected. This oligomerisation has been previously described in low power CW plasmas of acrylic acid. The similarities between pulsed 50W and 5W CW plasmas include gas phase chemistry, plasma polymer chemistry and deposition rates. This might suggest that the pulsed plasma environment is a continuation of the low power CW environment, but to lower average powers than can be sustained using a CW signal generator. Measurements of ion energies suggest a more complex system.

3:40pm PS1-ThA6 Control of Ion Energies in RF Plasmas used for the Surface Modification of Polymers, *D. Barton*, UMIST, UK; *J.W. Bradley*, UMIST, UK, U.K.; *D.A. Steele*, *R.D. Short*, University of Sheffield, UK

Despite the widespread use of low pressure (~10mTorr) radio frequency (13.56MHz) plasmas for the surface modification of polymers the importance of the various plasma species, e.g. positive ions and VUV photons, in effecting these changes remains the subject of some debate. To investigate the role of positive ions in the argon plasma treatments of various polymers, we have developed a technique which allows for the in situ control of the ion energies at the polymer surface. The technique does not perturb the bulk plasma, and in particular leaves the VUV flux unchanged. A further advantage is that that no grids or optical windows are

placed in front of the sample. The technique is similar in principle to the active compensation of Langmuir probes, in that it relies on feeding an RF signal onto the polymer which is phase and amplitude matched to the (RF) sheath potentials. By increasing the amplitude of this signal, we force the self-bias potential of the sample more positive and thereby reduce the ion energy at the polymer surface. This contrasts with the well known technique of biasing substrates with an unmatched RF signal which greatly increases ion energy to the surface. By varying the contribution from positive ions to the total energy deposition on the polymer surface, we are able to estimate the respective roles of ions and VUV in the surface modification of polystyrene, an important biomedical plastic. The effects of plasma exposure are measured by X-ray photoelectron spectroscopy, XPS. Although demonstrated for a particular plasma reactor, polymer and gas, the approach is generic and could be applied more widely.

### 4:00pm **PS1-ThA7 Surface Chemical Patterning by Plasma Polymerization**, *R.D. Short*, *N. Bullett*, *A.J. Beck*, University of Sheffield, UK; *C. Blomfield*, Kratos Analytical, UK

Plasma polymerization has been used to create chemically-patterned surfaces. The fidelity of the patterns is demonstrated by means of imaging TOFSIMS and XPS. The sequential plasma deposition of a hydrocarbon compound (1,7 octadiene) and a functionalized compound (allyl amine or acrylic acid) through electron microscope grids has been used to create surface patterns of amine and carboxyl, respectively, on polymer sheets. By this approach it has been possible to fabricated surfaces containing stripes of 75-150 microns and squares, of similar dimensions, of amine and carboxyl functionalities. These patterns have been used to spatially control protein adsorption, demonstrated using a fluorescent marker, and cell attachment and spreading.

#### 4:20pm PS1-ThA8 The Relationship between Deprotection and Film Thickness Loss during Plasma Etching of Chemically Amplified Resists, A.P. Mahorowala, D.R. Medeiros, IBM T.J. Watson Research Center

Positive-tone chemically amplified (CA) resists provide the sensitivity, contrast and resolution necessary to print state-of-the-art sub-wavelength features using KrF (248 nm) and more recently ArF (193 nm) lithography. These materials are also being looked at for printing sub-100 nm features with F@sub 2@ (157 nm) and next-generation lithography technologies such as EUV (13 nm) and E-beam projection lithography (EPL). Beyond the desired exposure-induced reactions, the acid-catalyzed deprotection reactions responsible for the solubility differential can also occur in unexposed resist areas when etched in a plasma due to uv-exposure, high energy ion bombardment, plasma composition and elevated substrate temperatures. Deprotection has been associated with resist mass loss and film shrinkage during plasma etch that can adversely affect the tight resist budget. In this paper, we determine the film thickness loss during etching of several unexposed CA resists in a variety of plasmas while simultaneously monitoring the film composition by FTIR. These results will be compared with theoretical predictions based on well-known deprotection mechanisms. It will be demonstrated that the acidic nature of certain plasmas such as Cl@sub 2@/O@sub 2@ can deprotect the resist film even in the absence of a photoacid generator (PAG). It will also be shown that the nature of the resist polymer and the identity of the deprotection products directly influence resist mass loss and etch rate linearity both of which can be controlled by careful selection of resist materials.

#### 4:40pm PS1-ThA9 Study of Defects Induced on Graphite Surface by Low Pressure Argon Plasma, A.L. Thomann, P. Brault, GREMI (CNRS), France; H. Estrade-Szwarckopf, B. Rousseau, CRMD (CNRS), France; C. Andreazza-Vignolle, P. Andreazza, CRMD (Universite d'Orleans), France

Since several years, we have been studying ultra-thin metal film deposition by a plasma sputtering method giving rise to low deposition rates (< 5 Å/min). Previous works have shown that the metal growth mode depends on the deposition conditions, which are tailored by the plasma conditions. For example, Pd metal has been found to form either 3D nanometer clusters, or very thin continuous layers.@footnote 1@ These results are interesting because they evidence that, with this deposition method, the film morphology may be easily chosen for a given application. Our aim is now to study how argon plasma pretreatment may modify the substrate surface state and thus, change growth modes. This will lead to an integrated plasma process allowing surface preparation followed by metal deposition. To study the induced defects, a plasma reactor has been added to an UHV-chamber equipped with STM, AFM, XPS and UPS analyses. This system allows chemical, electronic and morphological characterizations of the substrates before and after plasma treatments of different durations (30 s to 1 h). For these experiments, Highly Oriented Pyrolytic Graphite (HOPG) substrate has been used because it has been thoroughly studied as well as the surface defects created by ions beam techniques. First results show that small (D= some Å) and large (D= tens of Å) size defects are created on HOPG surface, that appear on STM images as hillocks of some Å height. Close to the large defects, a graphite lattice superstructure is observed. After a long lasting plasma treatment, the C1s XPS spectrum of the HOPG surface is completely modified ; on STM images, the hexagonal lattice is no longer observed and the superficial atomic structure appears as highly distorted although with a very small roughness (< 2 Å). @FootnoteText@ @footnote 1@ P. BRAULT et al, Recent Research Development in Vacuum Sci. And Technol., 2, R.A. Gottscho R.J. Pearton Eds. (Transworld Research Network, India, 1000).

#### 5:00pm PS1-ThA10 Novel Technique to Enhance Etch Selectivity of Carbon ARC over PR based on O@sub 2@/CHF@sub 3@/Ar Gas Chemistry, J. Hong, J.S. Jeon, Y.B. Kim, Samsung Electronics, South Korea; T.-H. Ahn, Samsung Electronics, South Korea, Korea

New Anti-Reflective Coating (ARC), amorphous carbon (C-ARC) substitute for inorganic ARC (SiON) is gaining attention recently in DRAM process as device scales down requiring more fine control of submicron (0.8) was achieved with annealing of amorphous carbon. The presence of hydrogen radical in the plasma produced similar result with C-ARC phase transition from sp@sub 3@ to sp@sub 2@ resulting from hydrogen-hydrogen abstract reaction. Deposition temperature of C-ARC determined hydrogen content on the surface. Hydrogen behavior on the surface appeared to be dominant factor to control etch selectivity and surface reaction mechanism of amorphous carbon will be discussed.

### Plasma Science and Technology Room 311 - Session PS2-ThA

#### Dielectrics I

Moderator: J.L. Cecchi, University of New Mexico

#### 2:00pm **PS2-ThA1 Ion Energy Control for Enhanced Plasma Etch** Selectivity, Y. Andrew, E. Ko, J. Machima, S.-B. Wang, A.E. Wendt, University of Wisconsin, Madison

Ion energy distribution (IED) control@footnote1@ at the substrate during plasma etching has been examined for improvements in SiO@sub 2@/Si and SiO@sub 2@/photoresist etch selectivity. The IED is controlled using a tailored bias voltage waveform applied to the substrate in place of the conventional RF sinusoidal waveform. A periodic waveform consisting of a voltage ramp in combination with a short pulse produces a plasma sheath in front of the wafer with nearly time-invariant voltage, leading to a nearly monoenergetic ion flux at the substrate, as compared to the relatively broad IED typically produced by a sinusoidal waveform. A 13.56 MHz helicon etching tool, equipped with a substrate bias power supply capable of producing the tailored substrate bias waveform, has been used to etch blanket films of photoresist, Si and SiO@sub 2@ using sinusoidal and tailored bias voltage waveforms. Etch rates of the blanket films are measured in situ using laser interferometry. Results to be presented show improved selectivity with the tailored waveform and a broadened process window for selective etching of SiO@sub 2@ over silicon in fluorocarbonbased plasmas, and etch rate vs. ion energy data suggest physical mechanisms. Selective etching of SiO@sub 2@ over photoresist is also examined, as it is very desirable to reduce the demand for thick photoresist and the challenge it presents to lithography technology. Substantial improvements in SiO@sub 2@/photoresist selectivity are expected. @FootnoteText@@footnote 1@S. B. Wang and A.E. Wendt, "Control of ion-energy distribution at substrates during plasma processing" to be published, J. Appl. Phys., June 1999.

#### 2:20pm PS2-ThA2 Temperature and Bias Effects in ICP Etching of Silicon Dioxide, *M.J. Cooke*, *G. Hassall*, Oxford Instruments Plasma Technology Ltd., UK

Silicon dioxide etching has been evaluated in a new induction-coupled plasma (ICP) source (designated ICP380), with particular attention to the sources of nonuniformity in etching 200 mm wafers. The contributions of the ICP source, the rf bias to the wafer, and the gas flow distribution to uniform etching are examined experimentally, supported by simple models. The implications for the design of etching hardware and for the protocols to achieve reproducible processes are considered. The rate of polymer deposition and etching in fluorocarbon plasmas has been measured as a function of the ion impact energy and the temperature of

the substrate, using interferometry and direct film thickness measurements. This has been related to the etch profile evolution for 10 micron deep trenches in thick silicon dioxide layers. It is shown that substrate temperature control is a necessary part of profile control, even for etches which are normally considered to be regulated by ion bombardment.

#### 2:40pm **PS2-ThA3 Control of Incident Fluxes and Surface Reactions in the Etching of Dielectric Materials,** *T. Tatsumi, M. Matsui, K. Kinoshita, S. Kobayashi, M. Sekine,* Association of Super-Advanced Electronics Technologies (ASET), Japan

The relationship between SiO@sub 2@ etch rates and the incident flux of reactive species in dual-frequency (27/0.8 and 60/2 MHz) parallel-plate systems were evaluated by using various in-situ measurements tools, such as infrared IRLAS, QMS, and OES. The thickness of a C-F polymer layer on the etched SiO@sub 2@ surface was measured by XPS. The SiO@sub 2@ etch rate depends on both the total amount of F in the C-F reactive species and the ion energy at a reactive layer on the SiO@sub 2@ surface.@super 1@ The net energy supplied to the reactive layer depends on the total amount of ions, the acceleration energy of ions (assumed to be the peakto-peak voltage, V@sub pp@), and the energy loss in the C-F polymer layer. The C-F polymer thickness increased when the incident flux of C-F species was relatively higher than the removal ability of C-F polymer, that mostly depends on oxygen flux. To vary the incident CF@sub x@ species, the C@sub 4@F@sub 8@ flow rate in the C@sub 4@F@sub 8@/Ar/O@sub 2@ was increased under 30mTorr of gas pressure and 1450 V of V@sub pp@. The ion flux was controlled by adjusting the RF powers. When we increased the ion flux from 3.0 x 10@super 16@ to 3.6 x 10@super 16@ cm@super -2@s@super -1@, the etch rate was increased because the energy on the reactive layer increased while the Si etch rate remained the same. Furthermore, the formation of the thick polymer (>1nm) started under higher C@sub 4@F@sub 8@ flow-rate conditions. This means the ability to remove excess C-F polymer on the etched surface was also improved. As a result the process-window of selective etching was increased. C@sub 5@F@sub 8@/Ar/O@sub 2@ gas chemistry was also evaluated in the same manner. An increase of C-concentration of the parent gas molecules induces the excess incidence of C atoms to the surface. As a result we mostly observed the C-F polymer deposition rate (not steady-state thickness) under high C@sub 5@F@sub 8@ flow-rate conditions. It is necessary to use the lower pressure or higher ion energy conditions to suppress the excess formation of the C-F polymer in the C@sub 5@F@sub 8@/Ar/O@sub 2@ process. @FootnoteText@ This work was supported by NEDO. @footnote 1@T.Tatsumi et al., J. Vac. Sci. Technol., A17 (1999) 1562.

#### 3:00pm PS2-ThA4 Reaction Mechanisms and SiO@sub 2@ Profile Evolution in Fluorocarbon Plasmas: Bowing and Tapering@footnote 1@, D. Zhang, University of Illinois at Urbana-Champaign; C. Cui, Applied Materials, Inc.; M.J. Kushner, University of Illinois at Urbana-Champaign

The rate and quality of fluorocarbon plasma etching of dielectrics is largely determined by a balance between deposition of polymer and ion activated chemical or physical sputtering. The proper balance results in selectivity and sidewall passivation producing straight walled features. The scaling of SiO@sub 2@ etching in fluorocarbon plasmas was numerically investigated using the Hybrid Plasma Equipment Model and the Monte Carlo Feature Profile Model (MCFPM). Algorithms were added to Surface Kinetics Module to account for multiple polymer layers, delivery of activation energy through polymer layers and ion activated polymer deposition. The MCFPM was also improved by including these processes. Reaction mechanisms were developed in which deposition of C@sub n@F@sub m@ radicals, either direct or ion activated, produces a polymer layer. At the interface of the polymer layer and SiO@sub 2@, a C@sub n@F@sub m@-SiO@sub 2@ complex is formed which, in the presence of fluorination by F atoms diffusing and ion energy delivery through polymer layers, produces etching in a 2 step process. Selectivity to Si results from lack of consumption of the polymer layer. SiO@sub 2@ etch rates increase with increasing bias at low biases due to increased activation energy delivered through a thinner passivation layer. Etch rates saturate at high biases due to polymer starvation. Comparisons to experiments showed that etch profiles transitioned from bowed to tapered as the passivation flux to ion flux ratio increased. This transition is delayed to higher passivation flux to ion flux ratios by increasing the bias. In general, loss of critical dimension correlated with a reduction in etch rate due to the thickening of passivation layers. For this reason, saturation of the etch rate due to polymer starvation also improved maintenance of the critical dimension. @FootnoteText@ @footnote 1@Work supported by AMAT, LAM, SRC and NSF.

3:20pm PS2-ThA5 Etching Mechanism of Silicon Nitride Film in Selfaligned Contact Etching Process, *M. Ito, S. Senda, K. Kamiya, M. Hori, T. Goto,* Nagoya University, Japan

For a contact hole etching process, the high etching selectivity of SiO@sub 2@ over Si@sub 3@N@sub 4@ as well as Si is required. In order to clarify the etching mechanism of Si@sub 3@N@sub 4@ film in H@sub 2@ diluted C@sub 4@F@sub 8@/Ar electron cyclotron resonance plasmas, we have investigated the mixing-layer in Si@sub 3@N@sub 4@ films using in-situ Xray photoemission spectroscopy and in-situ Fourier transform-infrared reflection absorption spectroscopy. From etching results and C-N bonding compositions in the mixing layer as a function of H@sub 2@ dilution ratio, the intensities of C-N sp@super 2@ bonds are considered to have a relation with the etching rate of Si@sub 3@N@sub 4@. On the other hand, C-N sp@super 1@ bonds were not observed at all in the films. Moreover, to clarify the H@sub 2@ dilution effect, we have observed the surface reaction during H@sub 2@ plasma annealing after etching Si@sub 3@N@sub 4@ films under C@sub 4@F@sub 8@/Ar plasma condition. It was found that intensities of C-N sp@super 2@ bonds as well as sp@super 3@ bonds decreased while Si-N bonds increased with the annealing time. Therefore, C-N sp@super 2@ bonds as well as C-N sp@super 3@ bonds are suggested to be etched through the formation of byproduct such as HCN and to be broken to form Si-N bonds through the recombination of the dangling bonds such as -N and -Si. This fact suggests that the restriction of reaction of C-N sp@super 2@ bonds and C-N sp@super 3@ bonds with H or F atoms is a key factor for achieving higher selective etching of SiO@sub 2@ over Si@sub 3@N@sub 4@.

3:40pm PS2-ThA6 High-performance Silicon Dioxide Etching for Highaspect Contact Holes, S. Samukawa, NEC Corp., Japan INVITED SiO@sub 2@ etching is done by using fluorocarbon gases to deposit a fluoropolymer on the underlying silicon. This deposit enhances the etching selectivity of SiO2 over silicon or silicon nitride. CF@sub 2@ radicals especially are used as the main gas precursor for polymer deposition. In a conventional gas plasma, however, the CF@sub 2@ radicals and other radicals (high-molecular-weight-radicals: C@sub x@F@sub y@) lead to the polymerization. This condition causes microloading and etching-stop in high-aspect-contact hole patterning due to the sidewall polymerization during SiO@sub 2@ etching processes. Conversely, by new fluorocarbon gas chemistries (C@sub 2@F@sub 4@/CF@sub 3@I), we achieved selective radical generation of CF2 and eliminated high-molecular-weightradicals. Under this condition, microloading-free and etching-stop-free high-aspect-ratio-contact-holes patterning of SiO@sub 2@ was accomplished. Thus, the higher molecular weight radicals play an important role in the sidewall polymerization in contact holes because these radicals have a higher sticking coefficient than CF@sub 2@ radicals. Selective generation of CF@sub 2@ radicals and suppression of C@sub x@F@sub y@ radicals are thus necessary to eliminate the microloading and etchingstop when formation high-aspect-contact-ratio holes.

4:20pm **PS2-ThA8 Selective Etching of SiO@sub 2@ in High Density Fluorocarbon Plasmas for Applications in Micro-systems**, *F. Gaboriau, M.-C. Peignon, G. Turban*, *Ch. Cardinaud*, CNRS-University of Nantes, France

In the recent years, plasma processes using high density sources have been extensively developed to meet the more and more stringent constraints required by integrated circuits fabrication. Among the various steps, dielectric etching is the more challenging as processes rely on polymerizing hydrofluorocarbon gases that produce simultaneously deposition and etching. It is thus difficult to achieve adequate SiO@sub 2@/mask etch selectivity and to continue etching in high aspect ratio features at the same time. Our aim is to develop new plasma processes concerning the oxide etching step for micro-machining device elaboration. Fabrication of MEMS (micro electro mechanical systems) and O-MEMS (optical MEMS) requires several conditions : i) a higher etch rate, ii) an extreme selectivity, iii) much longer etching processes. Previous studies have shown that adding methane to a fluorocarbon gas (CHF@sub 3@, C@sub 2@F@sub 6@, CF@sub 4@) yields to a significant improvement of the selectivity from 4 to 20 with no significant loss in the SiO@sub 2@ etch rate (300 nm/min). The present study using in-situ real time measurements by ellipsometry and quasi in-situ XPS analysis is focused on the influence of gas flow rate on the SiO@sub 2@ and Si (acting as a mask) etching using a mixture C@sub 2@F@sub 6@-CH@sub 4@. C@sub 2@F@sub 6@ was chosen due to a higher oxide etch rate compared to CHF@sub 3@ and CF@sub 4@. Increasing the gas flow rate when using pure C@sub 2@F@sub 6@ yields to an increase of both material etch rates ; the selectivity is thus unchanged and equal to 2. In contrast, using C@sub 2@F@sub 6@-CH@sub 4@ mixtures with 40% of methane leads to a significant

improvement of the selectivity (from 4 to 15) when increasing total gas flow rate ; indeed, oxide etch rate shows the same behavior as before whereas silicon etch rate decreases when increasing gas flow rate. Besides, XPS analysis exhibits a dependence between the silicon etch rate and the fluorocarbon layer thickness pointing out that this overlayer controls the silicon etching. Influence of the gas flow rate on the gas phase is under study using mass spectrometry, optical emission spectroscopy and Langmuir probe ; these diagnostics will allow us to determine the ion flux on the surface and to correlate the different evolutions of plasma species with the etch rate evolution for a better understanding of SiO@sub 2@ and Si etch mechanisms.

#### 5:00pm PS2-ThA10 Trench Etch Processes for Dual Damascene Patterning of Low-k Dielectrics, P. Jiang, F.G. Celii, W.W. Dostalik, K.J. Newton, Texas Instruments, Inc.; H. Sakima, Tokyo Electron America

The use of dual damascene patterning for integration of Cu with low-k dielectric films has introduced new challenges for plasma etch processes. With a via-first dual damascene approach, an important issue for trench etch is defect formation (i.e., oxide ridges) around vias which can degrade device reliability. The use of low-k films as the dielectric material adds additional complexity and more limitation on the etch process parameters. This paper discusses the development of etch processes that meet the special requirements for Cu/low-k dual damascene trench etch. All experiments were conducted in a medium-density TEL Dipole Ring Magnetron (DRM) system. The dielectric film used here was an organosilicate glass (OSG). Using C@sub 4@F@sub 8@/N@sub 2@/Ar chemistry, a trade-off was observed between etch rate and oxide ridge formation. The N@sub 2@/Ar ratio was found to be the key parameter in controlling the severity of the oxide ridges, but eliminating the ridges using the N@sub 2@/Ar ratio resulted in a low OSG etch rate and poor throughput. However, we will discuss an alternative method which achieves high OSG etch rate while maintaining CD control and ridge-free conditions. The effect of various process parameters on the OSG etch rate and ridge formation will be detailed. A comparison of experimental results against numerical simulations of C@sub 4@F@sub 8@-based bulk plasmas with varying gas flow ratios will also be reported.

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### Plasma Science and Technology Room 310 - Session PS-FrM

#### **Dielectrics II**

Moderator: S. Rauf, Motorola Inc.

8:20am **PS-FrM1 Pulsed-PECVD Organosilicon Films for Use as Insulating Biomaterials**, *H.G. Pryce Lewis*, Massachusetts Institute of Technology; *D.J. Edell*, InnerSea Technology; *K.K. Gleason*, Massachusetts Institute of Technology

Thin films produced by plasma-enhanced chemical vapor deposition (PECVD) have potential application as conformal coatings on implantable devices with complex topologies and small dimensions. Coatings on such devices need to be biocompatible, insulating, and flexible enough to minimize static forces on the surrounding tissue. In this study, we describe use of pulsed-PECVD to deposit thin films from the hexamethylcyclotrisiloxane (D@sub 3@). Pulsed-PECVD is a method in which plasma excitation is modulated to favor deposition from neutral and radical species. Thin, conformal coatings were demonstrated on nonplanar substrates suitable for implantation, such as copper wires and neural probes. Coatings were resistant to prolonged immersion in warm saline solution, and wire coatings produced by pulsed-PECVD showed more flexibility than analogous coatings deposited by continuous-wave (CW) excitation. Using Fourier Transform Infra-Red (FTIR) spectroscopy, it was demonstrated that the mode of plasma excitation is important in determining film structure. Both CW and pulsed-PECVD showed evidence of crosslinking via ternary (T) and guaternary (Q) silicon atoms bonded to more than two oxygen atoms. Methylene groups were observed only in CW films, and may constitute part of a carbon crosslinking unit of the form Si-(CH@sub 2@)@sub n@-Si, where n@>=@1. Methylene was not detectable in the pulsed-PECVD films, suggesting that formation of carbon crosslinks requires a longer plasma decomposition period. The presence of two distinct crosslinking structures in CW films leads to a highly networked structure and results in brittle coatings on thin wires. A higher proportion of terminal methyl groups was also observed in CW films, suggesting that pulsed-PECVD films may retain more precursor ring structure than CW films.

#### 8:40am PS-FrM2 Kinetic Suppression of Process Gas/Silicon Substrate Reactions During the Remote Plasma-assisted Deposition of Al@sub2@O@sub3@ and Ta@sub2@O@sub5@ on Hydrogen Terminated Silicon Substrates, *R.S. Johnson, H. Niimi, J.G. Hong, G. Lucovsky*, North Carolina State University

Deposition of alternative gate dielectrics such as Al@sub2@O@sub3@, Ta@sub2@O@sub5@, Zr(Hf)O@sub2@ and Zr(Hf)O@sub2@-SiO@sub2@ alloys onto H-terminated silicon by chemical vapor deposition, CVD, direct plasma-enhanced CVD, and/or atomic layer deposition, is generally accompanied by subcutaneous growth of interfacial SiO@sub2@ or metal silicate layers that significantly increase equivalent oxide thickness, EOT. Previous studies have shown that silicon substrate/process gas reactions could be effectively suppressed in remote plasma-enhanced CVD, RPECVD, of SiO@sub2@, Si@sub3@N@sub4@ and Si-oxynitride alloys by deposition reaction pathway control. Two aspects of RPECVD contributing to suppression of substrate reactions are i) downstream injection of silicon and metal atom precursors which prevents their fragmentation into reactive species in the gas phase, and ii) fast CVD reactions between unexcited precursors and upstream, plasma-activated oxygen with growth rates > 3-5 nm/minute. Substrate/process gas reactions have been studied by interrupted RPECVD processing-analysis cycles using on-line Auger electron spectroscopy, AES, in a UHV-compatible multi-chamber system. RPECVD of Al@sub2@O@sub3@ and Ta@sub2@O@sub5@ on Hterminated Si, using metal-organic precursors with deposition rates > 5.0 nm/minute effectively suppresses substrate/process gas reactions. Based on AES spectra and capacitance-voltage data, subcutaneous interfacial growth contributes less than 0.5 nm to EOT. In contrast, attempts to deposit ZrO@sub2@-SiO@sub2@ alloys by RPECVD from a Zr(IV)-tbutoxide source at significantly reduced deposition rates, < 1 nm/minute, leads to Si substrate/process gas reactions with Zr silicate subcutaneous interfacial layers adding ~ 1-2 nm to EOT.

9:00am PS-FrM3 Simulation and Dielectric Characterization of Reactive DC Magnetron Co-sputtered (Ta@sub 2@O@sub 5@)@sub 1-x@(TiO@sub 2@)@sub x@ Thin Films, J. Westlinder, Y. Zhang, F. Engelmark, H.-O. Blom, G. Possnert, S. Berg, University of Uppsala, Sweden

New capacitor material with high dielectric constant is needed for future integrated capacitor structures. Tantalum pentoxide (Ta@sub 2@O@sub 5@) is considered as one of the most promising candidates. By incorporating titanium into the Ta@sub 2@O@sub 5@ thin film, the already excellent electric and dielectric properties are believed to improve even further. In this work, thin films of (Ta@sub 2@O@sub 5@)@sub 1x@(TiO@sub 2@)@sub x@ have been grown utilizing reactive DC magnetron co-sputtering of tantalum and titanium in an argon/oxygen atmosphere. By varying the input power to the targets, the composition of the thin film can be controlled. The composition of the films was analyzed with Elastic Recoil Detection Analysis (ERDA) revealing the titanium oxide content (x ranging from 0 to 0.40). The dielectric constant, leakage current and breakdown voltage as well as the refractive index has been measured for different compositions and will be presented. The films are amorphous as-deposited, showing some degree of short range order. To be able to further investigate what influence that has on the dielectric properties of the material, films have been annealed at different temperatures. Data from both simulations and experiments of the dual-target reactive sputtering system will be presented.

# 9:20am PS-FrM4 Plasma Enhanced Chemical Vapor Deposition of Zirconium Oxide: Spectroscopic, Material and Device Characterizations, J.P. Chang, B. Cho, D. Bae, L. Sha, University of California, Los Angeles

As metal-oxide-semiconductor devices continue to shrink in dimensions, high dielectric constant materials such as zirconium oxide@footnote 1@ are needed in both transistor and capacitor structures for improved charge storage and reduced leakage current. In this work, zirconium t-butoxide (Zr(OC@sub 4@H@sub 9@)@sub 4@) is used with O@sub 2@ to deposit zirconium oxide on silicon in a high density Electron Cyclotron Resonance reactor. The gas phase reactions including the decomposition of precursors are investigated using optical emission spectroscopy (OES). Optical emission intensities from the atomic (Zr, C, O and Ar) and molecular species (ZrO, CH and CO) are recorded and quantified as a function of process parameters such as gas flow rates, process pressure, source power, and substrate temperature. Langmuir probe is used to determine the plasma potnetial, the electron density, n@sub e@, and electron temperature, T@sub e@. Various surface analysis techniques including X-ray photoelectron spectroscopy and X-ray diffraction are used to analyze the composition, chemical states, and crystalline structure of the deposited ZrO@sub 2@ films. These measurements are combined to propose realistic gas-phase and surface reaction mechanisms. The effect of in-situ postdeposition annealing on surface composition and film morphology is also investigated at 500-700°C in various ambient, including N@sub 2@, Ar, and O@sub 2@. NMOS transistors and MOS capacitors of a poly-Si(200nm)/ZrO@sub 2@/Si structure are fabricated and tested to determine the dielectric constant, leakage current, I-V and C-V characteristics of ZrO@sub 2@. Moreover, stress induced leakage current and time dependent dielectric breakdown are also investigated to determine the material reliability for the application of ZrO@sub 2@ in microelectronics. @FootnoteText@@footnote 1@ D. J. Hubbard and D. G. Schlom, "Thermodynamic stability of binary oxides in contact with silicon", Journal of Materials Research, 11(11), 2757(1996).

#### 9:40am **PS-FrM5 Etching of High-k Dielectric Zr@sub 1-x@Al@sub x@O Films in Chlorine-containing Plasmas**, *K. Pelhos*, *V.M. Donnelly*, *A. Kornblit*, *M.L. Green*, *R.B. Van Dover*, *L. Manchanda*, *Y. Hu*, *M.D. Morris*, *J.E. Bower*, Bell Laboratories, Lucent Technologies

As new, advanced high-k dielectrics are being developed to replace SiO@sub 2@ in future generations of microelectronic devices, understanding their etch-characteristics becomes vital for integration into the manufacturing process. We report on the etch rates and possible mechanisms for one such dielectric, Zr@sub 1-x@Al@sub x@O (x > 0.2-0.35), in plasmas containing a mixture of Cl@sub 2@ and BCl@sub 3@, as a function of gas composition and ion impact energy. Higher concentrations of BCl@sub 3@ enhance the etch rate as well as selectivity of Zr@sub 1-x@Al@sub x@O etching as compared to the etching of Si, whereas increasing ion energy increases the etching rates but decreases selectivity. In a high density helical resonator plasma, etching rates on the order of 700 Å/min and 1:1 selectivity are typical. Angle-resolved XPS was used to study the composition of the upper ~30Å of the film, before, during and at the end of the etching process. The as-deposited film is found to be enriched in

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Al near the surface (x>0.5). During etching the surface remains slightly Al enriched (5% over the bulk concentration). The adsorbed B concentration (>50at%) in the surface region far exceeds the gas phase composition (

#### 10:00am PS-FrM6 CVD BST (Ba@sub x@Sr@sub 1-x@TiO@sub 3@) Etching Characteristics in Inductively Coupled Ar/Cl@sub 2@ Plasma, *I.-Y. Kwon*, *H.-S. Shin*, *J.W. Kim*, Hyundai Electronics Industries Co. Ltd., Korea

We investigated the etching characteristics of CVD BST film with Ar/Cl@sub 2@ gas chemistry in ICP reactor. The changes of BST etch rate with various etching parameters such as gas mixing ratio, source power, bias power, pressure, and total flow rate were systematically examined. And, electron density, electron temperature, ion density, and plasma potential of Ar/Cl@sub 2@ plasma were measured with L/P, and also representative ions and neutrals in the plasma were analyzed by OES, RGA, and SIMS. XPS was employed for the surface analysis of BST film. Upon varying Ar/Cl@sub 2@ gas mixing ratio, the maximum BST etch rate was observed at 40% Cl@sub 2@. It was generally regarded that Cl@sub 2@ gas assisted BST etching chemically by the formation of some chlorides on the BST surface. XPS results showed that peak shifts including Ti, Ba, Cl were induced by the formation of chlorides. However, Ti remaining on the BST surface was decreased with increasing Cl@sub 2@ gas until 40%, and then saturated above 40% Cl@sub 2@. And, the changes of Ti, Ba, Sr and Cl ions and neutrals with Ar/Cl@sub 2@ ratio showed same saturation tendency by OES and QMS analysis. Therefore, it is estimated that the chemical etch portion of Cl@sub 2@ gas in BST etching is saturated at 40% Cl@sub 2@. On the other hand, ion saturation current decreased dramatically as the Cl@sub 2@ gas addition to Ar gas, and relative DC-bias and ion energy in plasma decreased with increasing Cl@sub 2@ gas above 40%. Therefore, it is also estimated that the physical sputtering with Ar/Cl@sub 2@ gas ratio rapidly decreases over 40% Cl@sub 2@ addition. Based on these results, it could be thought that the BST etch rate increases by chemical etch portion of Cl@sub 2@ gas under 40% Cl@sub 2@, and then is determined by physical sputtering above 40% Cl@sub 2@ due to the saturation of chemical etch portion. So, we propose chemically-assisted physical sputtering as a etch mechanism of BST film in Ar/Cl@sub 2@ plasma.

#### 10:20am **PS-FrM7 Hardmask Characterization for Polysilicon Gate Patterning, F.G. Celii,** C. Gross, S. Detweiler, B. Trentmann, K. Kim, W.D. Kim, H.-Y. Liu, R.T. Laaksonen, Texas Instruments, Inc.

To pattern sub-0.10  $\mu m$  structures required for next-generation poly-Si gates, advanced etch techniques must complement current lithography methods. One approach uses photoresist line-narrowing combined with an etch hardmask. The hardmask suitability is determined by the poly-Si etch resistance, the optical properties (if used as an anti-reflection coating (ARC) layer) and integration issues (e.g., cleanup and cost). We report the characterization of silicon-rich nitride (SRN) and silicon oxynitride (SiON) films used in poly-Si gate patterning. SiON and SRN films were deposited by PECVD in commercial 200 mm reactors. Film composition was measured by RBS and HFS spectroscopies. Typical SiON films contained ~40% Si and O, with ~20% H. Blanket films of 200 3000 Åthickness were characterized optically by FT-IR spectroscopy over 400 - 4000 cm@super -1@ and variable-angle spectroscopic ellipsometry (VASE), over 190 - 1000 nm. The VASE data provides optical constants at lithography wavelengths (193, 248 nm) of the various film compositions. We characterized patterned films by CD swing curves, in which in-line pre-etch critical dimension (CD) measurements are plotted vs. the photoresist (PR) thickness. Reflectivity minima below 1% were calculated using determined optical constants for PR/SiON/Si with SiON thicknesses at 325 Å and ~1000 Å. Etch properties and patterned profiles will also be summarized.

#### 10:40am PS-FrM8 Selective, Anisotropic and Damage-Free SiO@sub 2@ Etching with a Hyperthermal Fluorine Atom Beam, *D.B. Oakes*, *W.G. Lawrence*, *A.H. Gelb*, Physical Sciences Inc.

The SIA Roadmap for semiconductors calls for the introduction of neutral beam etching processes in future device generations. Specifically, neutral beam tools are required for silicon dioxide (SiO@sub 2@) etching in the formation of the gate dielectric and contact and via holes. The need for neutral beam tools arises from the combination of space-charge limitations on etch anisotropy and etch induced damage due to the charge content of the beam. The objective of this project is to demonstrate a neutral beam tool that selectively and anisotropically etches SiO@sub 2@. Physical Sciences Inc's FAST@super TM@ plasma technology was used to produce hyperthermal fluorine atom beams with tunable translational energy in the range, 1 to 15 eV. This unique technology accesses an energy range that can facilitate efficient, high rate etching of certain materials without the use of ions that produce damage. The SiO@sub 2@ etching study included

the first measurement of the velocity and temperature (20 to 200 C)dependence of atomic fluorine reacting with SiO@sub 2@ in the 1 to 10 eV translational energy range. The data suggests two reaction mechanisms contribute to etching under these conditions. Etching near 1 eV includes a significant thermal component while etching near 10 eV is dominated by a direct process, dependent on the fluorine atom translational energy. Under conditions in which the direct process dominates, anisotropic etching has been demonstrated. Both the selectivity and anisotropy of SiO@sub 2@ etching are dependent on the discharge chemistry. Selectivity ratios of 7:1 for SiO@sub 2@ etching versus both silicon and photoresist were demonstrated. Anisotropies of etching profiles exceeded 20:1. Future work will seek to improve both the selectivity and anisotropy of the process and will address scale-up of the tool for 300 mm wafer etching. Application of the FAST technology to low k dielectric etching based upon organic materials will also be discussed.

#### 11:00am PS-FrM9 A Downstream Plasma Etching Model Used to Describe the Etching Mechanisms of Low-k Polymers, *R.R.A. Callahan*, *G.B. Raupp*, *S.P. Beaudoin*, Arizona State University

Future integrated circuit manufacturing will require new materials to yield improved circuit performance and meet increasingly stringent environmental regulations. One novel material under current study is an organic polymer, parylene. Parylene is being investigated as an alternative low-k dielectric material because it offers both environmental and performance advantages over the current dielectric, silicon dioxide. From an environmental perspective, parylene-n is desirable because it can be etched using oxygen instead of perfluorinated compounds (PFCs) typically used for dielectric etching. This will reduce greenhouse gas emissions. From a performance point of view, parylene is a lower dielectric constant material than silicon dioxide. The use of parylene-n may ultimately reduce cross-talk and RC time delays. In lieu of reactive ion etching, downstream etching using a microwave source has been studied in order to characterize the etching mechanism without ion interactions for three different types of parylene; parylene-N, parylene-C, and fluorinated parylene. The apparent activation energy for the etching process has been observed to range from 6.41 to 7.64 kcal/mol at various pressure settings. Etch rate has been determined as a function of pressure ranging from 0.4 to 2.0 Torr and oxygen flow rate ranging from 25 to 225 sccm and applied plasma power of 250 watts. In addition to experimental work, the etching process has been modeled. The total model includes predictions of: 1) the velocity distribution in the afterglow region, 2) the oxygen atom concentration in the plasma, 3) the oxygen atom concentration in the afterglow region, and 4) the oxygen atom concentration at the surface of the sample. The model has been validated using nitrogen dioxide titration. The model validation, the model predictions, and their implications for parylene etching will be presented.

11:20am PS-FrM10 Surface Studies of the Etching of Low-k Hydrogen SilsesQuioxanes (HSQ) Dielectrics under Medium and High Density Plasma Conditions, C.N. Ho, Nanyang Technological University, Singapore; C.H. Low, P. Yelehanka, A. Cuthbertson, A. See, L.H. Chan, Chartered Semiconductor Manufacturing Limited, Singapore; G. Higelin, Nanyang Technological University, Singapore

The need for RC delay reduction, arising from device scaling and increased interconnect complexity, leads to the evolution of vast varieties of low-k inter-metal dielectrics. Doped oxide is the more established group being studied due to its similar composition as SiO@sub 2@. However, issues associated with the film stability, have to be resolved before successful integration of these materials into the multi-level interconnect scheme is achieved. In this work, the chemical aspect of the etching of FOx, one type of SiO@sub 2@-like HSQ materials, is evaluated as part of the feasibility studies towards successful low-k IMD integration. In our previous studies, it was demonstrated that FOx IMD vias can be successfully etched under both medium (MDP) and high density plasma (HDP) conditions. Comparative studies on physical performance were performed. Typically, less FOx sidewall bowing was observed in the case of HDP. In addition, higher FOx etch rate and less FOx removal during in-situ photoresist strip (PRS) can be observed. However, higher Si-H loss is induced as shown by FTIR studies. In this work, we perform surface studies using XPS techniques on patterned wafers etched with MDP and HDP source. The surface chemical composition of partially etched TEOS and FOx as well as the post-resiststripped etched surfaces is investigated through detailed peak deconvolution analysis. In general, higher C1s with negligible Si2p & O1s signal can be observed on both TEOS and FOx surfaces etched under HDP condition. This suggests the presence of a large amount of CF@sub x@ polymer. De-convolution of the C1s signal further indicates difference in

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the composition, particularly C/F ratio, of polymeric species formed under MDP and HDP condition. After O@sub 2@ treatment, significantly high Si2p and O1s signal can be observed, indicating oxidation of the etched surface. However, in-situ PRS exhibits additional capability in removing the polymer residues.

#### 11:40am PS-FrM11 Planar-Antenna Structure UHF-ECR Plasma for Highly Selective Insulator Film Etching, K. Yokogawa, M. Izawa, S. Yamamoto, N. Negishi, Y. Momonoi, H. Kawahara, M. Kojima, K. Tsujimoto, S. Tachi, Hitachi, Ltd., Japan

We developed an ultra-high-frequency ECR plasma (UHF-ECR) etching system with a planar-antenna structure for the etching of insulator film. We believe that high precision radical control, CF@sub 2@/F ratio and CF@sub 2@/ion ratio control of fluorocarbon plasma, is an important for etching of insulator film with highly selective and fine feature control for below 0.13  $\mu$ m design rule ULSI devices. UHF-ECR has a function of the radical control that is achieved by the plasma gap control for reduction of source gas dissociation and the double-near-surface effect @footnote 1@ for radical changes. A 450 MHz UHF wave was supplied to a planar-antenna located on the opposite side of a wafer. The magnetic field for ECR was supplied by solenoid coils, and distance between the planer-antenna and ECR plane was 5-20 mm. Stable plasma in a wide density range between 10@super 11@ and 10@super 12@ /cm@super 3@ was formed at pressure range between 1 and 50 mTorr. The plasma was uniform within ±3% up to a diameter of 200 mm, and the plasma distribution on the wafer was controlled by the magnetic-field distribution. The SiO@sub 2@ film etching was carried out by UHF-ECR plasma with C@sub 4@F@sub 8@ based gases. We confirmed that the increasing of CF@sub 2@/F ratio can be achieved by the plasma gap reduction using optical emission spectroscopy. We obtained self-aligned-contact etching with selectivity of 25, and high-aspect-ratio-contact hole etching (0.13 µm, aspect ratio: 14) with etching rate above 700 nm/min. High selectivity and high feature control ability were also demonstrated with low-k films such as organic SOG film and organic film. @FootnoteText@ @footnote 1@ S.Tachi, M.Izawa and M.Kojima; 1997 Proceeding of dry process sympo. p.83-90.

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