#### **Plasma Science**

#### Room 103 - Session PS1+MM-MoM

#### Science & Technology of Microplasmas and MEMS Processing

Moderator: M.G. Blain, Sandia National Laboratories

#### 9:40am PS1+MM-MoM1 The Challenges of Plasma Etching in MEMs Processing, G.R. Bogart, J.T.C. Lee, A. Kornblit, H.T. Soh, K.E. Teffeau, F.P. Klemens, J.F. Miner, Agere Systems INVITED

The rapid advancement in semiconductor technology has allowed for the design and manufacture of more complex microelectromechanical systems (MEMs). Tiny gears and simple microchannels have yielded to more complex integrated systems on a single chip. The applications of this new technology span multiple disciplines and accounts for the wider acceptance of these systems in the market place. While there are numerous methods to generate these micromachines, dry etching provides a level of manufacturing control that wet etching cannot deliver. Additionally, processes that were once limited to wet etching are now being asked of dry etching due to the added control. As an example, large ultra-thin membrane generation, while generally limited to wet etch processes, is now a possibility using dry etching techniques. For optical telecommunications components, the use of thin, silicon on insulator (SOI) wafers allows one to easily combine bulk micromachining with surface micromachining to generate well supported free standing structures. The new requirements that are being placed on dry etching processes have created issues that need to be handled in creative ways. Increasing aspect ratios with 90 degree sidewall angle specifications are competing against demands for higher etch rates, uniformity, selectivity, and other processing metrics. This paper will address some of the challenges that lie ahead for dry etching in the MEMs area.

#### 10:20am PS1+MM-MoM3 Maskless Etching of Silicon using Patterned Microdischarges, K.P. Giapis, California Institute of Technology, U. S. A.; M. Sankaran, California Institute of Technology

Hollow cathode microdischarges have gained recent attention for their high-pressure operation and intense UV radiation. Due to their non-Maxwellian electron energy characteristics, they are capable of producing excited states such as excimers and radicals. For this reason, these discharges could serve as a source of reactive species for materials applications. In this talk, we will present the operation of CF4/Ar microdischarges and their potential use in silicon etching. Because of the ability to form discharges in small holes and lines, we have used devices as stencil masks to transfer patterns directly into bare substrates. Devices employed were fabricated in copper-polyimide structures with hole diameters of 200  $\mu$ m. Discharges in flowing gas mixtures (25 sccm CF4 / 75 sccm Ar) were operated at 20 Torr with DC voltages less than 400 V and currents between 0.01-1 mA. Optical emission spectroscopy was used to detect the presence of etchants such as fluorine radicals. To etch n-type silicon (100), the 2-layer structure was patterned and pressed against the substrate. With the silicon as the cathode of the device, etch rates were found to be larger than 7  $\mu$ m/min. SEM images showed profiles with a peculiar shape attributed to the expansion of the plasma into the etched void. The plasma expansion was also monitored by I-V characteristics which showed an approximate linear increase in discharge current during the etch time. This technique has also been applied to etching arrays of multiple holes and lines with similar resulting etch rates and profiles. Maskless pattern transfer in this dimensional range presents an alternative to laser drilling and ultrasonic milling.

## 10:40am PS1+MM-MoM4 Efficiency of Microfabricated ICP Sources@footnote 1@, F. Iza, J.A. Hopwood, Northeastern University

Recently a micromachined 5 mm-inductively coupled plasma (ICP) source and its use in optical spectroscopy have been reported.@footnote 2,3@ The performance of this device in terms of ion density and power efficiency was poorer than expected in comparison with larger ICP systems. A simple model for micro-ICP sources suggested that increasing the frequency of operation and the coupling between the source and the plasma could lead to improved performance. New microfabricated devices operating at higher frequencies (690 MHz-818 MHz) and with improved coupling coefficients have been fabricated and characterized. Argon plasmas have been generated between 100 mtorr and 12 torr and have been sustained with as little as ~100mW. Probe measurements have been carried out to determine the ion density and electron temperature versus coupling coefficient, frequency, pressure and power. The electron temperature increases from 3 eV to 4.5 eV as the pressure decreases from 0.4 to 0.1 torr (53.3~13.3 Pa) independently of the frequency of operation and power absorbed by the device. Improved coupling coefficients lead to ion densities of 9x10@super 10@ cm@super -3@ at 400 mtorr while consuming only 1W. This ion density is three times larger than in previous micro-ICP sources under the same conditions. Increasing the frequency from 690 MHz to 818 MHz, however, does not increase the efficiency as predicted by previous models. A new model that incorporates the power dependence of the plasma resistance will be presented to explain this behavior. @FootnoteText@ @footnote 1@This work is supported by the NSF under Grant No. DMI-0078406. @footnote 2@J.Hopwood, O. Minayeva, and Y. Yin, "Fabrication and characterization of a micromachined 5 mm inductively coupled plasma generator", J. Vac. Sci. B 18, 2446, (2000). @footnote 3@O. Minayeva, and J.A. Hopwood, "Optical Emission Study of a Microfabricated Inductively Coupled Plasma", AVS 47th International Symposium, Paper MM-WeM4.

# 11:00am PS1+MM-MoM5 Microhollow Cathode Discharge Flow and Stability, D.D. Hsu, M.A. Nierode, D.B. Graves, University of California, Berkeley

The microhollow cathode (MHC) is a geometry used to sustain atmospheric-pressure glow discharges. Flowing gas through an array of MHCs could be used to process surfaces. For example, nitrogen gas can be flowed through a microhollow cathode discharge (MHCD) in order to incorporate nitrogen onto a polymer, such as polyethylene terephthalate. Convective gas flow through the MHCD is found to affect the stability of these discharges. For example, helium flow greater than 300 sccm through a 200  $\mu m$  hole at atmospheric pressure allows the MHCD to be sustained at a lower power than a stagnant helium discharge. In addition, the neutral temperature, measured by optical emission spectroscopy, of a heliumnitrogen discharge decreases when going from a stagnant discharge to one with gas flow. Higher flowrates of nitrogen through the hole cause the current to transition from a direct current to a pulsing current. The pressure drop across the hole and the gas flowrate suggest that Poiseuille flow can be used to model flow through an MHC. With pressure, peak temperature, and power deposition data, a fluid model of the discharge can help determine the spatial extent and temperature profile of the discharge. We will discuss the stability limits of these microplasmas as a function of power, pressure, gas flow, and gas composition.

#### 11:20am PS1+MM-MoM6 Experimental and Numerical Model Investigations of Miniature Microwave Plasma Sources, D. Story, T.A. Grotjohn, J.A. Asmussen, Michigan State University

In the past, the challenge in microwave plasma research was to develop techniques that provide high ion and free radical densities uniformly, over large and ever increasing process areas. Since scale-up was usually an important issue when considering industrial applications, the study of very small microwave plasmas, on the order of a few millimeters, was rarely done. Recently, interest in the development of systems on a chip, MEMS and their related micro system applications, has suggested the possibility of numerous applications for mini and micro plasma sources. Accordingly, this investigation is devoted to the development and the understanding of the behavior of very small microwave plasma sources. We have constructed two microwave plasma systems that create and allow for the experimental investigation of millimeter size plasmas. Plasma are generated across a wide range of input parameters, including pressure variation from below 1 Torr to 1 atmosphere, input power at 2.45 GHz from one watt to 100 watts, and a variety of gas mixtures including argon, nitrogen and hydrogen. Microwave plasma of various sizes (volumes) and aspect ratios are studied. Plasma density, size, shape, ignition, and emission spectra are monitored during each experiment to characterize the miniature plasma over the operating range. Companion global model and two dimensional numerical models will be developed and used to further understand the operation of miniature microwave plasma sources. The experimental and modeling results will identify the experimental operating regime necessary to excite and maintain stable, high density, miniature microwave plasma sources and will also identify the important figures of performance, such as electron temperature versus pressure/power and absorbed power densities versus pressure and plasma size.

## 11:40am PS1+MM-MoM7 Potential and Current Profiles of Nitrogen Gas DC Microplasmas, C.G. Wilson, Y.B. Gianchandani, A.E. Wendt, University of Wisconsin-Madison

We have recently reported on@footnote 1@ DC microplasmas which have been generated between patterned thin-film metal electrodes on the

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surface of a wafer. Typical operating pressure and power density are in the range of 1-20 Torr and 1-10 W/cm@super 2@, respectively. The plasma extent can be varied from 1 cm by variations in the electrode area, operating pressure and power. Silicon etch rates of 4-17 µm/min have been achieved. This technology allows multiple independent etching microplasmas to be operated on a single silicon wafer, enabling parallel or consecutive processing. Applications for this include trimming of electronic and micromechanical components, ranging from resistors to resonant gyroscopes. In this paper we will report on characteristics of microplasmas generated by co-planar in-situ electrodes. Breakdown voltage has been found to differ from the Paschen curve, being more uniform over a wider range of pressures. Contour plots of the floating potential of microplasmas have been measured, and the bulk of the voltage drop in the plasma column has been found to be proximate to the cathode. The floating potential is non-uniform at equal heights over the cathode and is lowest close to the center of the electrode. The height of the plasma column is found to scale with operating pressure, ranging in height from 3000-900 µm as pressure changes from 1.2-6 Torr. The internal voltage drop in the plasma column is considerable, and varies with the power density and pressure. At lower pressures, the current is found to be denser at the outer edges of the electrodes, and at higher pressures the current moves to the inner edges, becoming more uniform as the power density increases. We explore the effects of these results on silicon etching performance. @FootnoteText@ @footnote 1@ C.G. Wilson, Y.B. Gianchandani, "Silicon Micromachining Using In Situ DC Microplasmas," Journal of Microelectricalmechanical Systems, Mar. 2001, pp. 50-54.

#### Plasma Science Room 104 - Session PS2-MoM

#### **Diagnostics I**

Moderator: A. Kond, Nagoya University, Japan

9:40am PS2-MoM1 Optical Emission Spectroscopy of Exhaust Stream Gases for Improved Process Control, G. Powell, Lightwind Inc.; C.T. Gabriel, Advanced Micro Devices

Traditional optical emission spectroscopy uses the processing plasma as the light source, limiting the application of OES to when the plasma is on. Another drawback occurs when OES is used in a plasma with a varying magnetic field, which induces signal variations that must be filtered out. We introduce here a new OES technique, where a small secondary plasma is added just downstream of the process chamber to provide a continuous OES light source. The secondary plasma generates emissions characteristic of gases flowing through the chamber or being emitted by the chamber. The monitoring can be carried out whether the main chamber plasma is on or off, giving an indication of chamber condition prior to processing a wafer. Signal oscillations from a moving magnetic field are completely removed by monitoring gases downstream of the chamber, simplifying data collection and interpretation for endpointing. Data from using the technique in a MERIE dielectric etch tool are given.

10:00am PS2-MoM2 Peak Wafer Temperature Measurements during Dielectric Etching in a MERIE Etcher, C.T. Gabriel, Advanced Micro Devices Using disposable instrumented SensArray APTI wafers, peak wafer temperatures were measured during plasma processing in a MERIE dielectric etch tool. An inorganic low-k dielectric etch process was studied, and many parameters were varied to determine their effect on wafer temperature. Wafer temperature rose rapidly when the plasma was turned on, approaching a stable temperature after about 30 sec. When the lower electrode temperature setpoint or the RF power setting was increased, wafer temperature increased linearly. Peak wafer decreased as backside He cooling pressure was increased. The dual-zone electrostatic chuck allows separate control of center and edge He pressure. These pressures were varied individually or together. Temperature measurements indicated that the zones give reasonably independent control of center and edge wafer temperature. The importance of monitoring and controlling wafer temperature during dielectric etching is also discussed.

10:20am PS2-MoM3 Spatially (z)-Resolved Electron Temperatures and Species Concentrations in Inductively-Coupled Chlorine Plasmas, Measured by Trace-Rare Gases Optical Emission Spectroscopy, V.M. Donnelly, Agere Systems; M.J. Schabel, Bell Laboratories, Lucent Technologies

Determining the spatial dependence of charged and neutral species concentrations and energies in inductively coupled plasmas (ICP) is important for understanding basic plasma chemistry and physics, as well as for optimizing the placement of the wafer with respect to the ICP source to maximize properties such as etching rate uniformity, while minimizing charging-induced damage and feature profile anomalies. We have determined the line-integrated electron temperature (T@sub e@) and Clatom number density (n@sub Cl@) as a function of the distance (z) from the wafer in a chlorine ICP, using trace rare gases optical emission spectroscopy (TRG-OES). The gap between the wafer and the window adjacent to the flat coil inductive source was fixed at 15 cm. The pressure was 2, 10, or 20 mTorr (95% Cl@sub 2@, 1% ea. of He, Ne, Ar, Kr, Xe) and the inductive mode power was 340 or 900 W. The % n@sub Cl@ (100% = full dissociation of Cl@sub 2@) increased with power and was highest in the region between mid-gap and the ICP window, reaching nearly 100% at 900 W. T@sub e@ measured by TRG-OES, characteristic mostly of the highenergy (>10 eV) part of the electron energy distribution function (EEDF), peaked near the source under all conditions except 2 mTorr and 900 W, where a maximum T@sub e@ of 5.5 eV was observed at mid-gap. The falloff in T@sub e@ away from the power dissipation region is mainly due to a preferential loss of high-energy electrons, sensed at high T@sub e@ conditions by a relative reduction in the intensity of higher energy Ar emission. We can explain this by both local and non-local effects: Electrons lose kinetic energy in reaching the higher potential energy regions of lower electron density near the wafer (non-local effect). At higher pressures, the mean free path for inelastic scattering by high-energy electrons becomes comparable to the reactor dimensions, causing the EEDF to be relatively hot at the source and cool at the wafer (local effect).

#### 10:40am PS2-MoM4 Diagnostic of Silicon Etch Plasmas by Optical and Mass Spectrometry, Correlation with XPS Surface Diagnostics, N. Sadeghi, University Joseph Fourier-Grenoble and CNRS, France; G. Cunge, R.L. Inglebert, L. Vallier, LTM/CNRS (CEA-LETI), France; O. Joubert, CNRS, France INVITED

As device dimensions are continuously decreasing, the precise critical dimension control during the etch processes becomes a key issue in device fabrication. A better understanding of both plasma composition and plasma-surface interaction during the process are required to obtain a deeper insight on etch mechanisms involved in plasma etching. This work is centered on polysilicon gate etch processes using HBr/Cl@sub 2@/O@sub 2@ and HBr/Cl@sub 2@/O@sub 2@/CF@sub 4@ chemistries in an inductively coupled DPS-5200 Applied Materials reactor. The chemical composition of the layers deposited on the trench sidewalls is analyzed by quasi-insitu XPS and is correlated to the relative densities of the different neutral species present in the gas phase and to the composition of the ions impinging on the wafer surface and on the reactor walls. The following conclusions can be drawn: - Contrary to the expectations, halogen ions are not the dominant ionic species impacting on the wafer surface. Mass spectrometry measurements show that in standard etch conditions, Si@super +@ and other silicon containing ions can account by more than 50% of the total ion flux. - In HBr/Cl@sub 2@/O@sub 2@ gas mixtures, the passivation layer is formed by redeposition of silicon etch products fragmented in the plasma and then redeposited on the feature sidewalls where they get oxidized by the oxygen present in the gas phase. When CF@sub 4@ is added into the gas mixture, the passivation layer is formed by condensation of CF@sub x@ species on the feature sidewalls. - Mass spectra experiments also give some interesting information on the influence of CF@sub 4@ addition in keeping the chamber walls clean. Consequences on real processes are discussed.

# 11:20am PS2-MoM6 Electrical and Plasma Property Measurements of a DRIE Bosch Process, I.C. Abraham, P.A. Miller, J.R. Woodworth, C.G. Willison, R.J. Shul, Sandia National Laboratories

We measured electrical and plasma properties of a DRIE (Deep Reactive Ion Etching) Bosch process used for micromachining bulk silicon. The DRIE process enables the patterning of high-aspect-ratio deep Si features using an iterative inductively coupled plasma (ICP) deposition/etch cycle in which a polymer etch inhibitor is conformally deposited over the wafer during the deposition cycle. The polymer deposits over the resist mask, the exposed Si field, and along the sidewall. During the ensuing etch cycle, the polymer film is preferentially sputtered from the Si trenches and the top of the

resist mask due to the acceleration of ions perpendicular to the surface of the wafer. Provided that the ion scattering is relatively low, the polymer film on the sidewall is removed at a much slower rate, thus minimizing lateral etching of the Si. Both the 2 MHz ICP source and the 13.56 MHz cathode components of the floating-potential oscillations (and therefore the plasma-potential oscillations) were measured by a glass-enclosed capacitive probe immersed in the plasma. We used rf-potential and current sensors installed at the output of the chuck's matching network and a calibrated equivalent circuit model to compute the chuck potential waveform. The plasma density and electron temperature were measured using a floating double Langmuir probe. Measurements were made throughout the etch and deposition cycles of the Bosch process. Estimates of the ion energy distribution are presented. This data is expected to increase understanding of the DRIE Bosch process and ultimately improve process control. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the Department of Energy under Contract DE-AC04-94AL85000.

#### Surface Engineering Room 132 - Session SE-MoM

Nanocomposites, Multilayers, & Nanostructured Materials Moderator: G.J. Exarhos, Pacific Northwest National Laboratory

9:40am SE-MoM1 Magnetron Sputtered W/C Films with C@sub 60@ as Carbon Source, J.-P. Palmquist, Uppsala University, Sweden; M. Oden, Zs. Czigany, J. Neidhart, L. Hultman, Linköping University, Sweden; U. Jansson, Uppsala University, Sweden

Thin films in the W-C system have been prepared by magnetron sputtering of W with co-evaporated C@sub 60@ as carbon source. We have previously demonstrated epitaxial growth of several binary and ternary metal carbides as well as superlattice structures and gradient films at very low deposition temperatures (100-500 oC). In this study, we present the first results of epitaxial deposition of several phases in the W-C system. In addition, nanocrystalline tungsten carbide films can be deposited. At low C@sub 60@/W ratios, epitaxial growth of @alpha@-W with a solid solution of carbon was obtained on MgO(001) and Al@sub 2@O@sub 3@(0001) at 400 oC. The carbon content in these films (10-20 at%) was at least an order of magnitude higher than maximum equilibrium solubility and gives rise to an extreme hardening effect. Nanoindentation measurements showed that the hardness of these films increased with the carbon content and values as high as 35 GPa were observed. At high C@sub 60@ /W ratios, films of the cubic @beta@-WC@sub 1-x@ (x = 0-0.6) phase was deposited. This phase is not thermodynamically stable at T< 2500 oC but is frequently observed in thin film deposition. The microstructure of the @beta@-WC@sub 1-x@ films was dependent on the deposition conditions. At high deposition rates, nanocrystalline films with a grain size <30 Å were obtained in the temperature range 100-800 oC. The hardness of these films varied from 14 to 24 GPa. Also, for the first time, we have demonstrated epitaxial growth of single-crystalline @beta@-WC@sub 1-x@ films on MgO(001) at very low deposition rates, ~5 Å/min. Finally, at intermediate C@sub 60@/W ratios, epitaxial films of hexagonal W@sub 2@C was deposited on MgO(111), while polycrystalline phase mixtures was obtained on other substrates.

#### 10:20am SE-MoM3 Synthesis and Characterization of Thermally Stable TiB@sub 2@/TiC Nanolayered Superlattice Coatings for Dry Machining Applications, K.W. Lee, Northwestern University, US; Y.H. Chen, Y.-W. Chung, K. Ehmann, L.M. Keer, Northwestern University

It was demonstrated from previous studies that nanolayered superlattice coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such superlattice coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800 â€" 1000 C regime or higher. For this reason, TiB@sub 2@ and TiC were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates included silicon, M2 steel and WC cutting inserts. Superlattice coatings with TiB@sub 2@ (001) and TiC (111) preferred orientations on Si (001) were synthesized. Transmission electron microscopy studies showed

that the layer structure of the coating was preserved after annealing in vacuum at 1000 C for one hour. Room-temperature hardness of these coatings approaches 50 GPa, far exceeding the rule-of-mixture value. Coatings synthesized using the substrate rotation system have improved surface smoothness and reduced internal stress. Wear and durability tests on coated M2 steel and WC cutting inserts demonstrated the improved tribological performance of these coatings under unlubricated conditions compared with other standard coatings such as TiN.

# 10:40am SE-MoM4 Chemical Vapor Deposition and Characterization of TiO@sub 2@ Nanoparticles, W. Li, S.I. Shah, C.P. Huang, University of Delaware; O.J. Jung, Chosun University, South Korea

Chemical vapor deposition (CVD) was used to deposit TiO@sub 2@ nanoparticles with and without metal ion dopants. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) experiments confirmed the TiO@sub 2@ chemical composition. X-ray diffraction (XRD) patterns showed the polycrystalline anatase structure of TiO@sub 2@. Transmission electron microscopy (TEM) revealed that these particles are nanosized with an average diameter of approximately 20-30 nm. The nanosized particles can provide a large surface to volume ratio and large number of free surface charge carries which are crucial for the enhancement of photocatalytic activity. In order to improve the photocatalysis efficiency, Pd@super 2+@, Pt@super 2+@, Nd@super 3+@ and Fe@super 3+@ transition metal ion were also incorporated as dopants. The effects of dopants on photocatalytic kinetics were investigated by studying the degradation of 2-chlorophenol (2CP) with an ultraviolet light source. The results showed that doped TiO@sub 2@ nanoparticles have higher photocatalytic efficiency than those without dopants with Nd3+ showing the highest efficiency. Time of 90% destruction of 2CP was reduced by one half with Nd3+ doping when compared with undoped TiO@sub 2@.

#### 11:00am SE-MoM5 Nanocomposite Tribological Coatings with "Chameleon" Surface Adaptation, A.A. Voevodin, J.S. Zabinski, Air Force Research Laboratory INVITED

Composite coatings where hard nanocrystalline grains are embedded in an amorphous matrix provide considerable improvement in hardness. toughness, wear resistance, and friction reduction. A review of their design concepts is provided with a focus on: (1) improvement in toughness characteristics; and (2) adaptive tribological behavior. Embedding small 5-20 nm hard nanocrystalline grains in an amorphous matrix helps to arrest crack development and introduces ductility through grain boundary sliding. Matrix materials may be selected to provide adaptation of the surface chemistry and/or microstructure to variations in environment and loading conditions to mantain tribological properties. Such materials have been coined chameleon coatings. A combination of nanocrystalline TiC and WC embedded into an amorphous diamond-like carbon (DLC) matrix enabled the coatings to adjust their mechanical response from hard to ductile and significantly reduced the danger of brittle failure. A similar concept was used to improve toughness of composite coatings made of nanocrystalline yttria-stabilized zirconia (YSZ) embedded in an amorphous YSZ/Au matrix. In another example, a combination of nanocrystalline WC and WS2 in an amorphous DLC matrix exhibited surface chemical and microstructural selfadjustment in sliding contact when test environment was cycled from humid to dry. This coating could repeatedly adjust its surface from hexagonal WS2 for sliding in dry nitrogen or vacuum environments to graphitic carbon for sliding in humid air, maintaining a low friction coefficient in both environments. The YSZ/Au nanocomposite developed a gold rich surface layer during heating at 500 °C in air, which considerably improved YSZ tribology in temperature cycling. This coating was further doped with MoS2 and carbon to obtain an environmental adaptation similar to that in the WC/DLC/WS2 system. Chameleon coating designs and applications for advanced tribological coatings are discussed.

#### 11:40am SE-MoM7 Nanometer-size Monolayer and Multilayer Molecule Corrals on HOPG: A TOF-SIMS, XPS and STM Study, Y.J. Zhu, T.A. Hansen, S. Ammermann, J.D. McBride, T.P. Beebe, Jr., University of Utah

The surface chemistry of highly oriented pyrolytic graphite (HOPG) bombarded with energetic Cs@super +@ ions was studied using the combined surface analysis techniques of TOF-SIMS, (time-of-flight secondary ion mass spectrometry), XPS (x-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). Controlled surface modification and defect production were achieved by bombardment of HOPG with Cs@super +@ ions at various energies and at various dose densities. XPS shows cesium implanted into HOPG exists in an oxidized state. The Cs@super +@ bombardment of HOPG enhances oxygen adsorption due to

both the dissociative adsorption of oxygen at defect sites produced by Cs@super +@ ions, and by the formation of cesium oxide. The surface coverage of cesium on HOPG increases linearly with increasing Cs@super +@ dose density at low bombardment energies, and decreases rapidly with increasing Cs@super +@ bombardment energy due to cesium implantation below the surface. The thermal stability of cesium in HOPG has a complex behavior at elevated temperatures. Defects created by Cs@super +@ ion bombardment in HOPG were subsequently oxidized at 650 @super o@C in air to controllably produce nanometer-size monolayer and multilayer molecule corrals (etch pits). Multilayer pits can be produced using higher energy Cs@super +@ ion bombardment, and monolayer pits can be produced using lower energy Cs@super +@ ion bombardment. The pit density, pit yield, pit diameter and pit depth can be controlled by varying experimental conditions, and they were studied systematically by STM. The measured depth-resolved growth rates for multilayer pits are in good agreement with the model of the growth rate acceleration by adjacent layers. The results obtained lead to a better understanding of the kinetics and mechanism of the graphite oxidation reaction, and more importantly to the accurate production and control of nanometer-size monolayer and multilayer molecule corrals on HOPG.

## Monday Afternoon, October 29, 2001

#### Plasma Science Room 103 - Session PS1-MoA

#### Plasma-Surface Interactions I

Moderator: S. Han, University of New Mexico

2:20pm PS1-MoA2 In-vacuo Electron-Spin-Resonce Study on Fluorocarbon Films for SiO@sub 2@ Plasma Etching, K. Ishikawa, S. Hayashi, M. Okigawa, S. Kobayashi, M. Sekine, M. Nakamura, Association of Super-Advanced Electronics Technologies (ASET), Japan; S. Yamasaki, T. Yasuda, J. Isoya, Joint Research Center of Atom Technology (JRCAT), Japan

An in-vacuo electron spin resonance (ESR) setup opens the new experimental approach to the understanding the microscopic chemical reactions in etching process. Creation of dangling bonds (DB), namely, bond breaking, is indeed a key process for etching mechanism and created DB are playing an important role for surface reactions. The in-vacuo  $\ensuremath{\mathsf{ESR}}$ technique is applied to the studies of surface, on which fluorinated carbon (a-C:F) film exists, during fluorocarbon gas etching processes of an amorphous SiO@sub 2@ film. In this work, we prepared a capacitivelydriven reactor which is connected with an ESR system through a wafer transfer system. An a-C:F film was deposited on a crystalline Si substrate with 20 nm thickness which is estimated using cross-sectional transmission electron microscopy. The carbon DB signal in a-C:F film was observed after transferring to the ESR cavity under vacuum ambient. This signal are stable as long as the sample is kept in vacuum, however, once the sample was exposed to air, the signal intensity drastically decreased. The decrease of ESR intensity by air exposure points out that the oxygen molecules penetrate deeply into the a-C:F film, and terminate spin centers in the film. This technique can be applied to the reaction of a-C:F films with oxygen atoms with a bottom layer of SiO@sub 2@ films for the case of SiO@sub 2@ etching processes, the selectice etching mechanisms. @FootnoteText@ This work was supported by NEDO.

#### 2:40pm PS1-MoA3 The Deposition on and Etching of Si(100) by Large, Hyperthermal Fluorocarbon lons, L. Hanley, E.R. Fuoco, M.B.J. Wijesundara, University of Illinois at Chicago

Fluorocarbon plasmas are commonly used to etch features into Si wafers for the production of microelectronic circuits. It has been postulated that large fluorocarbon ions participate in both etching the Si and deposition of a fluorocarbon thin film on Si that hinders etching.@footnote 1@ We study the ability of mass-selected beams of large, hyperthermal fluorocarbon ions to deposit films on and etch Si(100). 25 to 200 eV C@sub2@F@sub4@@super+@ and C@sub3@F@sub5@@super+@ ions are deposited H-Si(100) and x-ray photoelectron spectroscopy is used to analyze the resultant fluorocarbon films. The disappearance of the Si(2p) peak in the survey spectra indicates that lower energy C@sub3@F@sub5@@super+@ ions create a continuous, relatively thick film as ion fluence is increased. On the contrary, higher energy C@sub3@F@sub5@@super+@ ions create a film that is self-limiting. As the ion fluence is increased, the film thickness stays constant. The C(1s) core level spectra contain the same fluorinated carbon components at all energies. comparison of two different ions, А C@sub2@F@sub4@@super+@ versus C@sub3@F@sub5@@super+@, show close similarities in the C(1s) core level spectra leading to the conclusion that the identity of the ion does not significantly change the chemical composition of the deposition. Atomic force microscopy is also employed to view the morphology change of the different energy deposits. These results are discussed in terms of the role of large fluorocarbon ions in the plasma etching of Si(100). @footnote 1@M.B.J. Wijesundara, Y. Ji, B. Ni, S.B. Sinnott, L. Hanley, J. Appl. Phys. 88 (2000) 5004 and references therein

#### 3:00pm **PS1-MoA4 Gas-Phase Chemistry of SiN PECVD Process at Ambient Pressure**, **G.R. Nowling**, S.E. Babayan, X. Yang, M. Moravej, R.F. Hicks, University of California, Los Angeles

The plasma-enhanced chemical vapor deposition (PECVD) of silicon nitride films has been examined in an atmospheric-pressure, helium-nitrogen discharge. The concentrations of the active nitrogen species in the afterglow have been determined by optical emission and absorption spectroscopy. For operation with 752 Torr N2 and 8 Torr He, at 32.9 (W/cm^3) RF power, and a 40.4 L/min flow rate, the plasma produced 4.8x10^15 cm^-3 of N, 2.1x10^13 cm^-3 of N2(A), 1.2x10^12 cm^-3 of N2(B), and 3.2x10^9 cm^-3 of N2(C). As the gas enters the afterglow, the concentrations of the active molecular nitrogen species drop by at least

two orders of magnitude. However, the ground-state atomic nitrogen atoms remain at a high concentration due to their slow rate of recombination by three-body collision. Spectroscopic measurements made of the gas and surface during PECVD indicate that the dominant reaction pathway is heterogeneous, i.e., occurs on the surface of the silicon nitride film. A numerical simulation has been developed which models the coupled fluid dynamics, gas-phase kinetics and surface reaction kinetics. These results together with the experimental measurements will be presented at the meeting.

#### 3:20pm PS1-MoA5 Study of Surface Reaction of SiO@sub 2@ Etching by Plasma Beam Irradiation, K. Kurihara, Y. Yamaoka, M. Sekine, M. Nakamura, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for Si/SiO@sub 2@/SiN etching to achieve high etching performance. The SiO@sub 2@ etching mechanism has been studied for the last three decades by using etching reactors and beam apparatuses. Multi-beam (ions and/or radicals) experiments are useful for understanding the surface reaction by simplifying beam-surface interaction. However, the plasma surface reaction in the etching reactor is very complicated because of many kinds of ions and radicals especially for fluorocarbon gas case. We have constructed a plasma-beam irradiation apparatus to examine the plasma-surface reactions under a real etching environment. Our plasma source can control plasma parameters, such as ion energy, residence time of introduced gases, radical/ion composition, and the ratio of a neutral flux to an ion flux. Desorbed products from the SiO@sub 2@ substrate were measured by a quadrupole mass spectrometer (QMS) during CF@sub 4@/Ar gas mixture plasma beam irradiation. The desorbed products from SiO@sub 2@ are assumed to be SiFx, COFx, (x=1-3), CO, CO@sub 2@ etc. However, SiFx and COFx can not be detected separately by QMS because they have the same atomic mass. Therefore, CF@sub 4@ gas which consists of isotope C@super 13@ was used as an etching gas in order to discriminate between SiFx and COFx. It was found that major Si containing desorbed products were SiF@sub 2@ and SiF@sub 4@. Their composition, furthermore, did not strongly depend on the ion energy in the range from 300eV to 800eV. After the plasmabeam irradiation, the surface of the substrate was examined by an in-situ XPS analysis. The fluoro-carbon (CF) layers on the SiO@sub 2@ were very thin, about 0.1-0.2 nm. The thicknesses of CF layer and their properties (F/C ratio and binding states) were found to be not dependent on the ion energy. This work was funded by NEDO.

#### 3:40pm **PS1-MoA6 Plasma Polymer Deposition and Permeation into Porous Substrates**, *S. Datta, J. Zhao, J. McDaniel,* Procter & Gamble; *S. Mukhopadhyay, P. Joshi,* Wright State University

Plasma polymerization for surface modification is gaining increased attention for industrial applications. Commercial efforts are focused, for example, on creating barrier coatings on food packaging and film-type substrates. However, another class of materials that can benefit from surface modification processes is porous substrates such as non-woven materials and woven fabrics. These materials are important for both consumer and industrial applications. Plasma polymerization is viewed as a surface modification process, that generally alters the top one micron layer of material, with no impact on bulk properties. However, for porous substrates such as fabrics and non-wovens, plasma polymerization of external as well as internal surfaces within the bulk material are important. To date, there have been few studies focused on the permeation of plasma polymerization through porous materials. This study was aimed at understanding the impact of various processing as well as substrate parameters on the permeation of plasma polymerization into porous materials. Cellulose-based filter paper was used to investigate the deposition profile and penetration of plasma treatment through porous materials. Several five or ten layer stacks of filter paper, each having different particle detention rating (different pore size) were used as model porous substrates. Plasma polymerized perfluoromethylcyclohexane (PFMCH) was deposited on these stacks and subsequent analysis of each layer in the stack was performed using X-ray photoelectron spectroscopy (XPS), contact angle measurements and water absorption rates. Correlation between these quantities will be discussed in light of the microstructure of these papers as seen by optical and electron microscopy. The dependence of plasma penetration depth upon (a) plasma parameters, (b) filter paper pore size and (c) duration of plasma treatment will be presented. @FootnoteText@ @Footnote \*@J. Zhao - Current address : March Instruments, Concord, CA.

## Monday Afternoon, October 29, 2001

4:00pm PS1-MoA7 Mechanisms for Surface Interactions of NH@sub x@ Radicals During NH@sub 3@ Plasma Processing of Metal and Polymer Substrates, C.I. Butoi, Primax, Inc.; M.L. Steen, E.R. Fisher, Colorado State University

The chemistry occurring at surfaces of substrates during plasma processing of polymers and metal surfaces is complex. For example, ammonia plasmas have been used to increase adhesion properties between metals and other materials and to create hydrophilic surfaces. We have examined interactions of NH and NH@sub 2@ radicals with different substrate materials during NH@sub 3@ plasma processing. NH@sub 2@ scatter coefficients, S, were obtained as a function of applied rf power (P) for polymer, silicon, and metal substrates. In most cases, S @>=@ 1, indicating NH@sub 2@ surface generation occurs at the plasma-substrate interface. Energy transfer between NH@sub 2@ and substrates was evaluated via translational temperatures for scattered NH@sub 2@ molecules, @THETA@@sub Tsc@. Translational temperatures for NH@sub 2@ molecules scattered from Pt, Cu, and Si substrates show little dependence on P, while NH@sub 2@ scattered from polymers have linear increases in @THETA@@sub Tsc@, changing by as much as ~120 K for P = 50-150 W. S and @THETA@@sub Tsc@ values measured using an ion-free molecular beam indicate ions increase both kinetic energy and amount of scattered NH@sub 2@. Examination of possible reaction pathways suggests that H atom abstraction by NH radicals may contribute to the observed surface generation of NH@sub 2@. Surface reactivity measurements for NH radicals on polymer surfaces show S < 1, consistent with this mechanism. The effects of P, substrate material and the presence of ions on NH surface interactions are presented, providing additional insight into the underlying mechanisms for NH@sub 3@ plasma processing of both polymer and metal surfaces. These surface interaction data will be presented along with mass spectral data and surface analysis, thereby providing a fairly comprehensive view of the ammonia plasma processing system.

4:20pm PS1-MoA8 Plasma Chemistry, Plasma-surface Interaction, and Surface Reactions during a-Si:H and a-SiN@sub x@:H Deposition, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands, Netherlands; E.R. Fisher, Colorado State University; E.S. Aydil, University of California, Santa Barbara; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands INVITED

Insight into the growth mechanism of plasma deposited materials is essential for full optimization and complete exploitation of the opportunities of plasma assisted deposition. Unraveling the growth mechanism requires investigation of the three different aspects of the deposition process: the plasma chemistry, the plasma-surface interaction, and the surface reactions converting surface species into bulk film. In this presentation, these three aspects will be considered and illustrated by studies on the radical dominated deposition process of hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-SiN@sub x@:H). From mass spectrometry and spectroscopic studies, the plasma species and their production and loss mechanism in plasmas of SiH@sub 4@ and mixtures with N@sub 2@ and NH@sub 3@ will be considered. From the density of the different species in the plasma their contribution to film growth has been determined. The surface reactivity and the reactions of the SiH@sub x@ and NH@sub x@ radicals on the surface will be treated as investigated by the laser-induced fluorescence (LIF) based "imaging of radicals interacting with surfaces" (IRIS) technique and the newly developed timeresolved cavity ring down spectroscopy (@tau@-CRDS). The nature of the surface during deposition and its connection with the surface reactions will be discussed using in situ attenuated total reflection infrared (ATR-FTIR) measurements of the chemisorbed SiH@sub x@ and NH@sub x@ surface hydrides. From the combination of results and the relations with the material properties, the kinetic growth models of the materials will be reviewed and further refined and extended.

#### 5:00pm PS1-MoA10 Arc Generation from Sputtering Plasma-Dielectric Inclusion Interactions, C.E. Wickersham, J.E. Poole, A. Leybovich, J. Fan, L. Zhu, Tosoh SMD, Inc.

Arcing during sputtering and etching is a significant cause of particle defect generation during device fabrication. The size of the dielectric inclusion plays a major role in determining if arcing occurs and particle defects are generated. We studied the effect of inclusion size, material type and plasma conditions on the propensity for arcing during sputtering of aluminum targets. We have found that there is a critical inclusion size required for arcing to occur. The critical size for Al@sub 2@O@sub 3@ inclusions in an aluminum target under typical magnetron sputtering conditions is 440  $\pm$  160  $\mu$ m. Inclusions with sizes above this critical value readily induce arcing and macroparticle ejection during sputtering.

Inclusions below this critical size do not cause arcing or macroparticle ejection. High-speed videos were used to study the arc initiation and behavior. The effect of inclusion aspect ratio and inclusion material type such as SiO@sub 2@, TiO@sub 2@, Al@sub 2@O@sub 3@, CaO, Ta@sub 2@O@sub 5@, AIN and BN on the arcing behavior of aluminum targets were also studied. When the inclusion size exceeds the critical value the sheath over the inclusion is deformed by the charge accumulating on the dielectric inclusion and the plasma positive column distorts toward the target leading to a bipolar arc. Inclusions below the critical size do not distort the sheath to an extent great enough to permit bipolar arc formation. Our proposed model predicts that the critical inclusion size depends upon the sheath thickness, which ranged between 300 and 600  $\mu m$  for the experimental conditions used in this study.

#### **Plasma Science**

#### Room 104 - Session PS2-MoA

#### **Plasma Modification of Organics**

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

#### 2:00pm PS2-MoA1 Treatment of Bone Tissue using an Inductively Coupled Plasma, C.Y.M. Maurice, J.H.R. Feijen, E. Stoffels, G.M.W. Kroesen, Eindhoven University of Technology, The Netherlands

Nowadays, the frontiers between physics, chemistry and biology are disappearing: polymer films are deposited via plasma processes, and numerous applications for medical purposes are emerging every day. However, the actual consequences of plasma interactions with organic matter have not yet been resolved. One of the interesting plasma applications is the possibility of refined modification of bone tissue. In this work we investigate the impact of positive ions formed in a low-pressure plasma on the bone surface. The sample is subjected to controlled ion bombardment and the post treatment response is investigated using microscopy. For plasma treatment we employ a low pressure Inductively Coupled Plasma (ICP) source. This type of reactor is capable of independently control the energy and the density of the positive ions impinging on the surface. At present, it is used for selective etching of inorganic samples. To monitor the ion energy, an energy resolved mass spectrometer is placed at the plane of the sample on the bombarded electrode and records the Ion Energy Distribution Functions. A Langmuir probe gives densities and potential measurements in the bulk plasma and the DSLIF (Doppler Shifted Laser Induced Fluorescence) technique gives access to IVDF's (Ion Velocity Distribution Functions) of the plasma ions. We characterise the plasma produced ions while processing the bone samples. This kind of treatment can have a large impact on the structure of the bone surface, such as reducing micro fractures, or selectively removing cancer cells. Understanding plasma-surface interactions under vacuum conditions may be useful in the future for the design of an atmospheric plasma source for bone treatment.

2:20pm PS2-MoA2 Nitrogen Uptake Kinetics of Poly(ethylene-2,6naphthtalate) Webs in Low-Radiofrequency Nitrogen Discharges, J.M. Grace, H.K. Zhuang, L.J. Gerenser, D.R. Freeman, Eastman Kodak Company Low-radiofrequency capacitively coupled nitrogen discharges are surprisingly effective at modifying the surface chemistry of polymeric materials. Such discharges are likely to have a variety of energetic species. Furthermore, the variety of interactions that such species may have with surface atoms in the repeat unit of a polymer such as poly(ethylene-2,6naphthalate) (PEN) is considerable. Hence, it is difficult to determine the dominant surface reactions responsible for the chemical modification. Nonetheless, it is helpful to examine the nitrogen uptake kinetics and compare them with inferred species fluxes to gain insights into the surface modification process. Using optical emission spectroscopy (OES) and ion flux probe (IFP) techniques, fluxes of atomic nitrogen and ions were measured in a relative sense over a range of discharge conditions. X-ray photoelectron spectroscopy was used to measure the nitrogen content of the PEN surface as a function of exposure time at given discharge conditions. The OES and IFP data suggest that applied power primarily controls the flux of ions to the substrate, while pressure primarily controls the flux of atomic neutral nitrogen. Using a surface sites model to interpret the nitrogen uptake data it is found that ion flux, neutral atomic nitrogen flux, and their interaction contribute to the nitrogen uptake rate, with the interaction term being quite significant. This apparent ion-neutral synergy suggests a two-step nitrogen incorporation process consisting of formation of a surface radical by ion bombardment (or by some other species whose flux scales with the ion flux), followed by reaction with atomic neutral

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nitrogen. In addition, direct reaction of atomic ions or atomic neutrals may contribute to the nitrogen uptake rate. Using the parameters obtained from analysis of the linear uptake regime, analysis of the surface saturation regime suggests that sputtering and recombination both contribute to loss of surface nitrogen.

## 2:40pm **PS2-MoA3 Control of Spatial Distribution of Adsorbed Proteins Using Plasma Surfaces**, *N.A. Bullett*, University of Sheffield, U.K.; *R.D. Short*, University of Sheffield, U.K., UK; *C.W.I. Douglas*, University of Sheffield, U.K.

The adsorption of proteins occurs whenever a material contacts with biological media. In cell culture, proteins rapidly adsorb to the plastic from serum and the adsorbed protein layer subsequently influences cell adhesion, proliferation and differentiation. The ability to control and direct specific protein adsorption and conformation would enable culture surfaces to actively influence the behaviour of cells. This work aims to show that we can exert a degree over control of the adsorption and conformation of proteins from both single solution and serum. The ability to control the spatial distribution of adsorbed proteins will also be demonstrated. Plasma-co-polymerisation of acrylic acid with 1,7-octadiene was used to create a range of carboxylic acid functionalised surfaces. Protein adsorption to these surfaces was measured using an antibody recognition technique (ELISA) and radio-labelling, FITC-labelling and XPS analysis of adsorbed proteins. For single protein solutions and serum, radio-labelling, FITC-labelling and XPS showed a decrease in the amount of adsorbed protein binding with surface acid content. ELISA results would appear to show the opposite, more protein binding to the acid functionalised surfaces. This apparent contradiction in data may be explained by a change in the nature of the adsorbed proteins. Chemical micropatterns were created by the plasma polymerisation of either acrylic acid or allyl amine onto 1,7-octadiene through TEM grid masks. Imaging ToF-SIMS and XPS was used to verify the chemical differentiation in the surface. The micropatterned surface was shown to influence the adsorption and spatial distribution of FITC-labelled adsorbed proteins.

#### 3:00pm **PS2-MoA4 Characterization of Pulsed Plasma Chemistry for the Deposition of Polyethylene Glycol-like Polymer Thin Films,** *D.C. Guerin,* Naval Research Laboratory, National Research Council; *D.D. Hinshelwood, V.A. Shamamian,* Naval Research Laboratory

We have deposited organic thin films with pulsed RF inductively coupled plasmas. We used two organic precursors, isopropyl alcohol and 1,4 dioxane, in argon. We characterized the plasmas with Langmuir probe measurements. Using in situ mass spectrometry, we identified the primary ionized species that diffuse to the surface. These species are different for the two precursors. We propose mechanisms for the creation of these species, which are primarily electron-impact dissociation ionization and ion-molecule reactions. Tuning the plasma parameters varied the mass distributions of the ionic flux to the surface. For example, at low pressure, the species due to electron-impact were predominant. We also used the mass spectrometer to measure the flux of neutral species to the surface. We determined that varying the plasma conditions has a large effect on the relative importance of ions and neutrals in the deposition process. At certain pressures and RF power levels, the flux of reactive neutrals is minor compared to the ion flux, which dominates the deposition process, X-ray photoelectron spectroscopy was performed on the samples. For isopropyl alcohol, a simple relation was discovered between the ion mass distributions and the chemical bonding character of the deposited film.

#### Plasma Science Room 134/135 - Session PS-MoP

## Plasma Diagnostics and Plasma-Surface Interactions Poster Session

#### PS-MoP1 Molecular Structure of Fluorocarbon Deposits Analyzed by EIMS and CIMS Combined with Thermal Desorption Technique, N. Takada, K. Sasaki, K. Shibagaki, K. Kadota, Nagoya University, Japan

In order to understand plasma-surface interaction in fluorocarbon plasmas. the analysis of fluorocarbon deposits is an important issue. To date, x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) are exclusively adopted for the analysis of fluorocarbon films. However, detail of the molecular structure of fluorocarbon films cannot be understood by XPS and FTIR. In the present work, we adopted electron-impact mass spectrometry (EIMS) and chemical ionization mass spectrometry (CIMS) for the analysis of the molecular structure of fluorocarbon films produced by C@sub 4@F@sub 8@ and C@sub 4@F@sub 8@-H@sub 2@ plasmas. A thermal desorption technique was used to evaporate fluorocarbon molecules from samples. In EIMS. thermally desorbed molecules were ionized by an electron beam with an energy of 70 eV. In CIMS, isobutene is ionized by electron impact to produce slow electrons. Negative fluorocarbon ions were produced via dissociative electron attachment of the slow electrons. The threshold temperature for thermal desorption of fluorocarbon molecules from a sample produced by a C@sub 4@F@sub 8@ plasma was 100-160 °C. Many peaks corresponding to mass numbers up to 800 were observed in the EIMS spectrum. The major peaks were classified into two groups having structures of CF@sub 3@(CF@sub 2@)@sub n@@super +@ and CF(CF@sub 2@)@sub m@@super +@. This result indicates that molecules desorbed from the sample contain the polymerized structure of CF@sub 2@. The overall shape of the CIMS spectrum of the fluorocarbon sample was similar to that of perfluorokerosene (PFK), which has a molecular structure of CF@sub 3@(CF@sub 2@)@sub n@CF@sub 3@. This suggests that fluorocarbon molecules desorbed from the sample have a molecular structure similar to PFK. By comparing the CIMS spectra of the sample and PFK, the mass number of the desorbed molecule was estimated to be 1100.

#### PS-MoP2 Real Time Analysis of the Remote Oxygen and Hydrogen Plasma Cleaning using Mass Spectroscopy, *H. Soh*, *H. Seo*, *Y. Kim*, *H. Jeon*, *Y.C. Kim*, Hanyang University, Korea

The plasma cleaning technologies have been attracting a great attention due to the demands of the compatible process with the most cluster tool and of the environmentally safe process. The photo resist (PR) ashing and PR strip processes are generally followed the silicon etching process to remove the PR and polymerized residues, respectively, during integrated circuit fabrication. However, the PR strip is the wet chemical process and causes environmental problems. Especially, the polymerized residues formed at the contact and via holes during the photo resist (PR) ashing and PR strip processes must be removed prior to the metal contact. In this study, we continuously monitored and systematically analyzed the volatile gases from the oxidized PR molecules during the low temperature remote plasma cleaning process. Mass spectroscopy (QMS200) was used for the real time monitoring of the volatile gases containing carbon and fluorine. In-situ Auger electron microscopy, X-ray photoelectron spectroscopy, atomic force microscope analysis systems were used to evaluate the cleaning effects and to avoid recontamination such as carbon absorption in the air. The surface morphologies of the samples before and after plasma cleaning were also observed using scanning electron microscope. This paper will present the oxygen and hydrogen remote plasma cleaning efficiency and its chemical reaction mechanisms. @FootnoteText@ @footnote 1@K.Sakuma, K.Machida, K.Kanoshida, Y.Sto, K.Imai and E.Arai, J.Vac.Sci. Technol.B 13(3), May/June (1995)

#### PS-MoP3 Investigation and Modeling of Plasma-Wall Interactions in Inductively Coupled Fluorocarbon Plasmas and the Effects of Chamber Dimension, E.A. Joseph, S.P. Sant, L.J. Overzet, M. Goeckner, University of Texas, Dallas; M.J. Kushner, University of Illinois, Urbana Champaign

Plasma-wall interactions in fluorocarbon based feedgas chemistries, namely CF4, are examined in both a standard and a modified inductively coupled Gaseous Electronics Conference (GEC) reference cell using In-Situ Fourier Transform Infrared Spectroscopy (FTIR). Initial measurements in the standard GEC reference cell show the dissociation of the CF4 feedgas into radical CFx species as has been observed elsewhere.@footnote 1@ Experimental results from both the standard GEC reference cell as well as the modified GEC reference cell, which differs from the standard cell in that it has easily configurable plasma exposed surfaces,@footnote 2@ are compared to results from the Hybrid Plasma Equipment Model@footnote 3@ to better elucidate the influence of the plasma exposed surfaces on plasma parameters including, but not limited to, plasma density, wall temperature, and CFx polymer thickness. @FootnoteText@ This material is based upon work supported by the National Science Foundation under Grant No. 0078669 @footnote 1@M. J. Goeckner, M. A. Henderson, J. A. Meyer, and R. A. Breun, J. Vac. Sci. Technol. A 12, 3120 (1994) @footnote 2@M. J. Goeckner, J. M. Marquis, B. J. Markham, and A. K. Jindal, Bull. Am. Phys. Soc. Vol. 45 No. 6 @footnote 3@R. Kinder and M. J. Kushner, J. Vac. Sci. Technol. A 19, 76 (2001).

#### PS-MoP4 Controllable Ion Source for Process Enhancement in a Downstream Plasma Ash Chamber, A.K. Srivastava, P. Sakthivel, I. Berry, Axcelis Technologies, Inc.; H.H. Sawin, Massachusetts Institute of Technology

Plasma ash tools have in the past been designed to generate a gentle downstream plasma impinging on the wafer. However, additional demands to remove residue, both in front-end and back-end processes have recently been imposed on these ash tools. This has led to a gradual transition of the old plasma asher into a ash-etch hybrid tool that can tolerate harsh etchants in moderate amounts, and also have the flexibility of controlling the ion flux to the wafer without charge damage. Different approaches have been attempted to meet these needs with limited success, mostly by taking the chamber towards the reactive ion etch (RIE) regime where the risk of device damage is high. A new approach to the dynamic control of ion generation and transport to the wafer, while maintaining operating regimes that are conducive to an ash tool and hence non-destructive to the wafer, is reported in this paper. In a typical downstream plasma ash tool. an upstream microwave discharge is fed into a plenum that disperses the reactive species through a hard-coated aluminum baffle plate above the wafer. When ion bombardment is required, a secondary ion source coupling radio frequency (RF) is switched on, creating a glow discharge in the plenum above the baffle plate. Under optimal conditions, electrons from the glow discharge are trapped inside the sheath of the baffle plate holes. These electrons complete the current path on the bottom surface of the baffle plate, and have sufficient energy to ionize some of the neutral gas. This secondary source of ions provides a gentle, low energy, uniform bombardment on the wafer. This paper describes the ion source in detail as it is used during specific ash/residue removal processes. The unique ion generation mechanism is discussed. Preliminary results of ion bombardment on the removal of the carbonized layer of implanted resist at low temperature are presented. Optical emissions data characterizing the ash chemistries are also presented.

#### PS-MoP5 A Multi-Technique Investigation of the Pulsed Plasma and Plasma Polymers of Acrylic Acid, Propanoic Acid and Hexamethylenedisiloxane, *S. Fraser*, *D. Barton*, University of Sheffield, England; *A.J. Roberts*, Kratos Analytical, England; *R.D. Short*, University of Sheffield, England, UK

The synthesis of thin plasma polymer films from radio frequency (rf) 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. Plasma polymers of acrylic acid, propanoic acid and hexamethylenedisiloxane have been fabricated from pulsed 13.56 MHz RF plasmas in a "capicatively" coupled plasma deposition chamber. Plasma "on" and "off" (t@sub on/off@) times in the millisecond (ms) pulse time regime have been investigated using a peak plasma power of 50 W. Employing a fixed ton (5ms) the effect of toff (0-2000 ms) on the solid-phase plasma polymer has been investigated using X-ray photoelectron spectroscopy (XPS) and timeof-flight secondary ion mass spectrometry (ToF SIMS). Mass spectrometry has been employed to monitor the neutral and charged species in the plasma-gas as a function of toff and deposition rates have been monitored by means of a quartz crystal mass balance (QCMB). For comparison continuous (CW) wave plasmas of equivalent "average power" have been studied. The XPS (C1s core line) show that with increased t@sub off@ the extent of functional group retention increased. Valence band XPS and SIMS data indicate at low "average" powers (0.2 W) a linear polymer, closely resembling the conventional polymer, is deposited. The mass spectral data indicate the principal affect of t@sub off@ is on the amount of intact monomer in the system. For example, with acrylic acid this was shown by

monitoring the signal from the molecular ion of acrylic acid (m/z 72) in the neutrals.

# **PS-MoP6** Synthesis and Characterization of New Material (BON) for Semiconductor Applications, G.C. Chen, S.-B. Lee, J.-H. Boo, Sungkyunkwan University, Korea

Recently, oxynitride compounds sparked among functional materials, such as Ti(ON), Si(ON) and SiBON. They presented a promising potential application of diffusion barrier, solar material and interlevel dielectric material. Since BON was declared as a by-product in synthesis of hard material, we have firstly developed the research on the molecular structure of new material (i. e. BON). In this study, we would like to report on the electrical property of BON thin films grown on Si(100) substrates by low frequency RF derived plasma assisted CVD. The effect of growth condition, such as flux of fed gas, deposition temperature as well as growth time, on the I-V characteristics are mainly discussed. The experimental results showed that the electrical resistance decreased with increasing the nitrogen flux and growth time. Amorphous BON thin film grown at relatively low temperature has more higher resistance than microcrystal containing thin film that obtained at high temperature, and the most smooth morphology was benefit of getting low resistance. By controlling nitrogen content in the film layer it can be possible to making the BON thin films that have either semiconducting or insulating properties. The asgrown new materials were characterized by XPS, RBS, FTIR, AFM, and TEM/TED. During CVD, moreover, the optical emission spectra (OES) were also measured in-situ for plasma diagnostics and analysing gas phase reaction. Based on the OES result, we confirmed that the formation of BON thin film was suit to be performed under nitrogen plasma.

#### **PS-MOP7** The Effect of Controlling the Ion Energies of a Plasma **Polymerised Deposition Surface Upon the Film Structure**, *D. Barton*, *R.D. Short*, University of Sheffield, UK; J.W. Bradley, UMIST, UK, U.K.

The formation of plasma polymerised films has been the subject of intensive research over many years. Despite this work and the technological relevance of such films, little attention has been paid to the actual mechanisms involved in both the polymer formation and deposition. In particular, the question of whether the polymer is formed either in the bulk plasma, the sheath region, or at the surface remains unresolved. We present an experimental technique which allows the independent control of positive ion energies at a deposition surface. The technique relies upon feeding an RF signal to the surface which is matched in both phase and amplitude to the RF potentials in the plasma. In this way, it is possible to control the energy of the positive ions at the surface, independently of other plasma parameters. Jons may be a significant constituent of polymer films as previous measurements of the ion flux to a deposition surface have suggested that these particles may be responsible for about 25% of the total polymer mass. Embedded into the deposition surface are plasma diagnostics including a plasma mass spectrometer, quartz mass balance and an ion flux probe. The deposited films are analysed using XPS. Using an acrylic acid monomer, we will relate energy changes of ions striking the surface to the film properties such as extent of cross linking and functionality retention.

#### PS-MoP9 Uniformity Control of Electron Temperature and Density within a Commercial-scale Helicon Plasma Processing Reactor, *M.J. Neumann*, *J.E. Norman*, *D.N. Ruzic*, University of Illinois at Urbana

A study of electron temperature and density profiles was performed with PlasmaQuest 256 helicon plasma processing research reactor to better understand power absorption within a plasma reactor operating in helicon mode. The plasma source is a PMT Mori 200 antenna, coupled with an inner and outer opposing magnetic field coil placed around the it and a third coil positioned below it. The use of external magnetic field coils gives the ability to quickly change from one operating mode and condition to another. External electrical and magnetic variation effects are observed with a radially and z-varying Langmuir probes and spectroscopy. For nitrogen at 800 W RF and 80 A on the inner and lower magnets, the electron density profile was seen to decrease inward from 1.1x10@super 11@ cm@super -3@ at the edge of the chamber to 6.0x10@super 10@ cm@super -3@ in the center, while the electron temperature increased inward from 1.0 eV to 4.8 eV at the center of the chamber. In contrast, at 800 W RF and 40 A on the inner magnet alone, the electron density profile was seen to increase inward from 2.0x10@super 10@ cm@super -3@ at the edge of the chamber to a peak of 7.0x10@super 10@ cm@super -3@, while the electron temperature decreased inward from 4.0 eV to 2.6 eV at the center of the chamber. Through manipulation of electron density and temperature, the surface properties of various biopolymers can be

changed, while leaving the underlying material unchanged. One observable change is a decrease in the water contact angle with common biopolymers, such as low-density polyethylene and high-density polyethylene. These changing plasma conditions have also been observed with argon and oxygen. Modeling has been performed to show the physical mechanisms involved in the electromagnetic energy transfer to the plasma. Thus, within the same reactor chamber and via only external manipulation, very distinct plasma conditions yielding different interaction properties can be produced.

#### PS-MoP10 Atomic-Order Plasma Nitridation of Ultrathin Silicon Dioxide Films, T. Seino, T. Matsuura, J. Murota, Tohoku University, Japan

Atomic-order nitridation of SiO@sub 2@ by a nitrogen plasma without substrate heating has been investigated using an ECR plasma apparatus. A 3nm-thick SiO@sub 2@ was thermally grown by wet oxidation of Si(100) at 700@super o@C. The SiO@sub 2@ film was nitrided by the nitrogen plasma for 1-324 min at the N@sub 2@ pressure of 1.3-2.6Pa with the microwave power of 200W. After plasma nitridation, some samples were annealed at 400-800@super o@C for 1hour in nitrogen. The depth profile was obtained by the repetition of etching by a 1%-diluted HF solution and XPS measurements. When the incident ions were exposed directly on the surface, the number of the incident ions (the product of the ion density and the plasma exposure time) was 3x10@super 15@-9x10@super 18@cm@super -2@, and the N1s peaks were observed at 397-398eV and at 402eV. With increasing nitrogen plasma exposure time, the N1s peak at 398eV shifted to 397eV corresponding to Si@sub 3@N@sub 4@. By annealing at 400-800@super o@C after nitridation, the N1s peak at 402eV disappeared. The depth profiles for the N1s peak at 397-398eV were almost the same before and after annealing. By a shutter placed above the wafer, the number of the incident ions was suppressed to 5x10@super 14@-1x10@super 16@cm@super -2@ and the ion energy (below 20eV) became lower than that (below 30eV) without the suppression of the incident ions, and the N1s peak was observed only at 399eV. By annealing at 600-800@super o@C after nitridation, the N atom concentration at 399eV was decreased due to the diffusion of the N atoms. This result is similar to the thermal nitridation of SiO@sub 2@ by NH@sub 3@. It is also found that the N atom concentration was normalized by the number of the incident ions in spite of the ion energy and the radical density. From these results, it is considered that the nitridation is caused mainly by the incident ions. It is suggested that the ion energy changes the binding conditions of N atoms in SiO@sub 2@.

PS-MoP11 Plasma Processing Tests from a Large Area High Density Plasma Source Based on Electron Beam Ionization, D. Leonhardt, Naval Research Laboratory; S.G. Walton, D.D. Blackwell, National Research Council; 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) when the electron beam is magnetically collimated. The beam ionization process is also fairly independent of gas composition, capable of producing low temperature plasma electrons (T@sub e@ ~ 0.5eV in molecular gases, 1-2eV in atomic gases) in high densities (n@sub e@ ~ 10@super 9@-10@super 12@ cm@super -3@).@footnote 1@ A 'Large Area Plasma Processing System' has been developed which consists of a planar plasma distribution generated by a sheet of 2-5kV electrons injected into a neutral gas background. The electron beam is magnetically collimated by a 150 Gauss field and operates in a gas pressures of 20-100 mtorr. A photoresist (PR) ashing process was studied under various system conditions In order to test plasma processing capabilities and control over processing parameters. The process system consisted of pure O@sub 2@ or O@sub 2@/Ar gas mixtures interacting with PR coated silicon substrates which were exposed to the plasma on an rf biasable (capacitively coupled) stage. Process conditions such as gas mixture composition, operating pressure, beam-to-substrate distance, duty cycle and incident ion energy were varied to determine the various effects of this plasma source on the PR ashing process. In situ Langmuir probe and mass spectrometry data@footnote 2@ are correlated to the material removal as determined by ex situ surface analysis (profilometry, SEM). Results show that the material removal process is ion energy dependent and highly anisotropic for ion energies @>=@50eV. Uniformity tests of the large area source will also be presented if time permits. Work Supported by the Office of Naval Research. @FootnoteText@ @footnote 1@D. Leonhardt, et al., AVS 47th Annual Symposium, Boston, MA, PS1-MoA5. @footnote 2@See presentation by S. G. Walton, et al., at this conference.

**PS-MoP12 Energy Distributions of Ions and Neutrals from a Sputter Source, G.J. Peter,** Inficon Limited, Principality of Liechtenstein, Liechtenstein; N. Mueller, H. Zogg, Inficon Limited, Principality of Liechtenstein

The kinetic energy of the deposited particles impinging on the surface of the substrate is an essential process parameter in sputter deposition processes. The energy as well as the mass of these particles can be measured with an energy selective mass spectrometer. lons from the plasma can directly and easily be guided by an Ion Transfer Optics into the energy and mass filter resulting in a high sensitivity. In contrast to this, neutral particles have to be ionised first, before any energy or mass filtering can be done. It is common to use electron impact ion sources with well defined electrical potentials for ionisation, although this is a low efficiency process. For optimisation of the sensitivity for neutral particles, a wide acceptance angle of the ion is mandatory. This can be obtained by minimising the distance between the entrance aperture and the ion source. But this design is in no way optimum for the detection of ions, as at least the ion formation chamber of the ion source is a poor ion optics. So any design of a combined instrument will result in a poor sensitivity for the ions and a high sensitivity for the neutrals and vice versa. In order to overcome these difficulties, an otherwise standard plasma process monitor PPM 422 was equipped with two exchangeable, electrically insulated entrance apertures. One of it was used for the measurement of ions and the other one for detection of neutrals. The electrical insulation allows to set the aperture to any electrical potential. So a realistic simulation of the potentials on the substrate ca be performed. The energy distributions of particles from a gun type planar magnetron were measured with this modified device.

#### **PS-MoP13 Species Characterization in Inductively Driven Fluorocarbon Etch Plasmas, G.A. Hebner**, Sandia National Laboratories, usa; *I.C. Abraham*, Sandia National Laboratories

A number of techniques have been used to characterize etching plasmas containing fluorocarbon gases. Laser induced fluorescence was used to measure the spatially resolved SiF and SiF@sub 2@ densities in inductively driven discharges containing C@sub 2@F@sub 6@ and C@sub 4@F@sub 8@. Measurements of the spatially resolved SiF and SiF@sub 2@ densities were performed as functions of the induction coil power, pressure, and bias power above a silicon surface. The SiF density had a maximum at a radial distance of 2 - 3 cm from the center of the plasma, and then monotonically decreased towards the edge of the plasma region. The SiF@sub 2@ density had a maximum at a radial distance of approximately 7 cm from the center of the plasma. Electron and negative ion densities was measured in C@sub 4@F@sub 8@ and the identity of the negative ions in C@sub 2@F@sub 6@, CHF@sub 3@ and C@sub 4@F@sub 8@ containing discharges was investigated using a novel photodetachment experiment. To investigate the influence of surface material, the rf biased electrode was covered with a silicon wafer or a fused silica (SiO@sub 2@) wafer. In most cases, the trends in the electron and negative ion density were independent of the wafer material. A novel microwave resonant cavity structure was developed to identify the negative ions using laser photodetachment spectroscopy. Unlike traditional microwave cavity techniques, this method offers the possibility of spatial resolution. This work was supported by SEMATECH and the United States Department of Energy (DE-AC04-94AL85000).

## PS-MoP14 Investigation on the Plasma Uniformity in Reactive Gas ECR Plasmas, *M. Shindo, Y. Kawai,* Kyushu University, Japan

Reactive gas plasmas are widely used in etching process for fabricating ULSI. In order to reduce the production costs, a uniform and high-density plasma with a large diameter is required. An ECR plasma can be a candidate for such a plasma, since it easily reaches more than 10@super 12@cm@super -3@. In addition, one of the mechanism of the uniformity in an Ar ECR plasma was clarified by Ueda and Kawai.@footnote 1@ On the other hand, the transportation and diffusion mechanism in reactive gas plasmas become complicated since a large quantity of negative ions are produced. Thus, it is necessary to investigate the plasma uniformity under the existence of much negative ions. In this study, an attempt to measure the spatial distribution of charged species in O@sub 2@/Ar and C@sub 4@F@sub 8@/Ar ECR plasmas was made. Here, the density of negative ions was estimated from the phase velocity of the ion acoustic waves (fast mode) which were launched from a wire antenna to which the positive pulse voltages (30µ sec in duration time and V@sub pp@=40V) were applied, and were detected with a plane Langmuir probe biased at -90V. The detected signals were observed with an oscilloscope, and a trough and a crest were found, corresponding to the waves excited at the leading and

falling edge, respectively. As a result, the negative ions existed near the wall rather than the center region. Moreover, it was found that the positive ion density was uniform in the center region, and the uniform area widened as the reactive gas mixture rate was increased. @FootnoteText@ @footnote 1@Y. Ueda and Y. Kawai, Appl. Phys. Lett.71 (1997) 2100.

#### **PS-MoP16 A Novel Approach to Time Resolved Langmuir Probe Measurements**, *A.K. Jindal*, *S.K. Kanakasabapathy*, *M. Goeckner*, *L.J. Overzet*, University of Texas at Dallas

Langmuir Probes, when used carefully, have provided spatially resolved plasma density, potential, and electron temperature measurements. However, time resolved Langmuir Probe measurements are time consuming in triggered box car averaged systems. We present a novel approach to time resolved Langmuir Probe I-V curve acquisition. Probe Current and voltage are measured as functions of time, for a fixed applied DC bias, with a digitizing oscilloscope. These traces are collected and a new applied bias is set. By doing this repeatedly, we build up I-V-t profiles. Then, in an offline fashion, time is eliminated between these various traces and I-V curves are obtained for all instances of time in the pulse period. In contrast to state of the art triggered box car averaged systems, I-V curves are obtained with better time resolution and much faster. For example: I-V curves for 512 instances of time within a 1 msec pulse period with 300 points in voltage, is obtained in as little as 15 minutes. Once these time resolved I-V curves are obtained, appropriate probe theory is used for extracting time resolved plasma parameters using a Levenberg-Marquardt@footnote 1@ fitting algorithm. The high speed of data acquisition minimizes the effects of long-term plasma drift associated with slower techniques. We shall be presenting data from pulsed Chlorine and Argon discharges using this technique. . @FootnoteText@ @footnote 1@W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery. NUMERICAL RECIPIES in C: The Art of Scientific Computing. Cambridge University Press. .

#### PS-MoP17 Evaluation of Langmuir Probe Theories via Comparison with Microwave Interferometry and Plasma Oscillation Probe Methods in ICPs, J.D. Evans, F.F. Chen, University of California, Los Angeles; W. Zawalski, Hiden Analytical, Ltd., England

Measurements of plasma density (Np) are performed under identical conditions using microwave interferometry (MWI), plasma oscillation probe (POP) and Langmuir probes. Np via MWI is treated as the "known" result to which the other techniques are compared. Data is obtained in a chamber that lies downstream from a PlasmaTherm ICP source, over a wide range of parameters: Prf<1kW, Te=2-5eV, Np=10^10 - 10^12 cm^-3. Ne obtained via POP agrees well with MWI in relatively low-collisional regimes, as expected. I-V curves are acquired using Hiden Analytical's ESPion Langmuir probe, which employs broadband RF compensation via inline chokes and a compensation electrode. A variety of probe tip radii are used, which allows for a broad base of comparison. Conventional probe theories (OML, ABR and BRL) are used, as well as an approximation based on the assumption that the ion current (Ii) is determined mainly by the unipolar sheath expansion, whose thickness follows a modified Child-Langmuir (C-L-mod) law in which Ii is nearly proportional to Vo<sup>(4/3)</sup>, where Vo = |Vbias-Vplasma|. Different probe theories yield vastly differing values of ion density (Ni), whereas Te is reliably determined in most cases. In most cases the dependence of Ii with Vo agrees very well the C-L-mod law. Excellent agreement between Ni thus obtained and the MWI results is observed throughout the parameter range. However, it is also found that Hiden's ESPsoft algorithm, which employs OML theory that predicts li^2 proportional to Vo, yields values for Ne in good agreement with those of MWI and POP. Reasons for the success of the C-L-mod law in light of this apparent paradox are presented.

PS-MoP18 Electron Energy Control in an Inductively Coupled Plasma by Means of Induction Field Reversal, *H. Shindo*, Tokai University, Japan; *T. Urayama*, ADTEC Plasma Technology CO., LTD, Japan; *Y. Horiike*, The University of Tokyo, Japan; *S. Fujii*, ADTEC Plasma Technology CO., LTD, Japan

In the deep submicron etching for ultra large-scale-integrated circuit (ULSI) processes, the development of low-pressure and high density plasma sources has been highly required. In these plasmas, however, several crucial problems have risen up in conjunction with electron energy. These are related to the fact that the electrons are prone to be excessively energetic in high density plasmas generated at low pressures. In this work, we studied electron energy control in an inductively coupled plasma by employing different azimuthal mode antenna. It is expected for electron energy to reduce at higher azimuthal mode antenna, because induction

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field is reversed with a shorter length. The experiments were carried out in an inductively coupled plasma (ICP) 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 three types of antenna were prepared.The electron temperature could be reduced by increasing the azimuthal mode number of one-turn antenna with no notable change in electron density. These effects were remarkable in low pressures below 10 mTorr, hence in a condition of longer electron mean free path. The mechanism for these behaviors is that the electron temperature at lower pressures depends on both the electron mean free path and the field reverse distance, as anticipated. The electron gains more energy with larger field reverse distance so long as the mean free path is same, and the electron mean free path is inversely proportional to the pressure. The RF magnetic field was also measured by a pick up coil, and its behavior was quite consistent with the electron energy, meaning that the electron energy change is not due to the capacitive effect. It was concluded that the induction field reverse distance in conjunction with electron free path was essential in electron energy control.

#### PS-MoP21 Novel In Situ Diagnostics for Plasma Processing of Advanced Materials, E.A. Evans, G. Zhang, University of Akron; A. Salifu, Cree Research

Kinetic and transport parameters for nitride growth and processing are required for process design and optimization. A new approach for accurately determining these parameters at processing conditions will be presented. We have combined a large inductively coupled plasma reactor with a digital microbalance to make measurements of substrate weight during plasma processing of aluminum and aluminum nitride samples. The current set-up is capable of sensing growth and/or etch rates on the order of 1 microgram per second regardless of substrate area. We will present results that demonstrate the usefulness of these measurements for understanding the kinetic and transport mechanisms involved during plasma processing. These relationships are important not only for controlling oxidation during and after deposition but also for identifying growth regimes for high quality thin film nitride materials.

## PS-MoP22 Analysis of Chlorine-Containing Plasmas, G.F. Franz, Infineon Corp., Germany

Capacitively coupled discharges of strongly reactive atmospheres containing mixtures of boron trichloride and chlorine are investigated employing impedance measurements, Langmuir probe measurements, optical emission spectroscopy (OES), and self-excited electron resonance spectroscopy (SEERS). The analysis covers the whole area spanned by these gases (including some mixtures), discharge pressure and RF power over more than one order of magnitude, and their impact on important plasma parameters like plasma density, plasma potential, electron temperature, temperature of the plasma bulk, electron collision rate with neutrals, and actual RF power coupled into the discharge. From these, other properties (electrical conductivity, capacitance, plasma bulk resistance, sheath resistance and its thickness) can be derived. Since the methods are partially complementary, a mutual control of the obtained data is made possible, and the limits of the methods can be evaluated. 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 ions could be found in the plasma which is referred rather to the effective cooling of the Cl-containing species than to the nonexistence of these species. Furthermore, we compared values for the electron temperature and the plasma density obtained with OES and SEERS, respectively, and with the Langmuir-probe system. The concordance in both properties is surprisingly good, despite the fact that the electron energy distribution should be described with two temperatures and only Langmuir is spatially resolved. The variation of the calculated dc conductivity either from impedance measurements or combined Langmuir/SEERS lies within a factor of 2 and is mainly referred to uncertainties of the current path rather than to principal faults of the various methods.

PS-MoP23 Fluorocarbon Decomposition Products and Effluent Analysis from Atmospheric Pressure Dielectric Barrier Discharges, S.F. Miralai, S. Mukhopadhyay, Wright State University; V. Shanov, University of Cincinnati; S. Datta, Procter & Gamble

Dielectric barrier discharges (DBDs) are gaining increased attention as an economical and reliable method for generating non-equilibrium plasma conditions in atmospheric pressure gases. This has led to a number of important applications including industrial ozone generation, surface

modification of polymers, excitation of CO2 lasers and large area plasma flat panel displays. One of the challenges in the development of applications of DBD is an understanding of reactive species generated in the plasma and analysis of effluent gases. Some of the reaction products in the effluent gases are in very low concentration, increasing the complexity of the detection process. This paper deals with the detection of reactive species and products in the plasma and in the effluent gases from a fluorocarbon dielectric barrier discharge plasma . Dissociation efficiencies of fluorocarbons at various frequencies and using different carrier gases , such as helium, nitrogen, argon and oxygen will be presented. Analysis of the reactive species and products will be described, using Optical Emissions Spectroscopy (OES) and Quadrupole Mass Spectrometry. Correlation of experimental data with preliminary modeling results will be presented.

#### PS-MoP24 Endpoint Detector for Controlling Clean and Passivation in HDP-CVD Processes, *R. Rulkens*, Novellus Systems, Inc.

Optical Emission Spectroscopy was used to develop a sophisticated End Point Detector for the clean and passivation steps of HDP CVD processes. During the clean process steps, NF3 plasma removes build-up of SiO2 on the reactor walls. The end point detector in real time determines the optimal time at which the silica film is removed from the reactor walls and prevents over or under etching. After the clean steps, a Hydrogen plasma is used in the passivation step to remove residual fluorine. In a similar manner, the End Point Detector determines the optimal time needed for passivation. The diagnostics are incorporated into the equipment hard- and software and automatically control the correct timing of the clean and passivation steps.

## Tuesday Morning, October 30, 2001

#### Plasma Science Room 103 - Session PS1-TuM

#### **Diagnostics II**

Moderator: V.M. Donnelly, Agere Systems

#### 8:20am PS1-TuM1 Radical Concentrations and Temperatures in a Dual-Frequency Capacitive Reactor Determined By Broad-Band UV-Visible Absorption Spectroscopy, J. Luque, E.A. Hudson, Lam Research; J.P. Booth, Ecole Polytechnique, France

Broad-band UV-visible absorption spectroscopy is next in simplicity to optical emission spectroscopy. Unlike optical emission, it provides direct information about ground states of neutral species in plasma environments. However, it has rarely been implemented as diagnostic in industrial plasma reactors. In the present work, we report measurements in a Lam dielectric etch reactor (27/2 MHz dual frequency capacitive) during semiconductor processing using Ar/C@sub x@F@sub y@/O@sub 2@ feedstock gas mixtures. Using a deuterium lamp source and a photodiode array detector we can measure absorption across the 200-260 nm region, allowing simultaneous detection of CF, CF@sub 2@ and SiF@sub 2@ radicals. Other species that we have detected include C@sub 2@ and C@sub 3@. We use the CF radical as example of this technique, and to illustrate the wealth of information easily extracted from moderately high resolution absorption spectra: CF radical ground state number densities are determined with a detection limit of ~10@super 10@ cm@super -3@ using off-the-shelf instrumentation. Typical densities are in the order of 10@super 13@ cm@super -3@ for a standard oxide etch recipe. CF rotational and vibrational temperatures are measured aided by spectral computer simulation code. Typical rotational temperatures, which are normally equivalent to gas temperature in the reactor, are in the order of 425 K. Vibrational distributions, with temperatures of 800 K, show nonthermalization compared to rotational temperatures. We found a previously unreported vibrational band, assigned as CF A-X(3,0), and it is heavily predissociated. Intensities of the CF A-X(v,0) and B-X(v,0) bands are used to determine accurate transition probabilities, enabling precise determination of concentrations and temperatures in future spectroscopic experiments via the CF A-X and B-X bands.

# 8:40am **PS1-TuM2 CF@sub x@ Kinetics, Gas Temperatures and Instabilities in a CF@sub 4@ Inductively-coupled Discharge, J.P. Booth,** H. Abada, P. Chabert, Ecole Polytechnique, France; G. Cunge, CNRS/LETI, France

The use of inductive discharges in fluorocarbon gases for SiO@sub 2@ etch applications has been hampered by narrow process windows and severe process drift problems, despite promising etch rate, selectivity and anisotropy results. We have extended our study of free radical kinetics in capacitively-coupled plasmas to these systems in order to investigate the origin of these problems. Laser-induced fluorescence was used to probe the axial concentration and temperature profiles and the kinetics of CF and CF@sub 2@ radicals in a pure CF@sub 4@ ICP. Rotationally-resolved LIF of CF shows that very high gas temperatures can occur (up to 1000K). Therefore, large gas temperature and density gradients exist within the reactor. The CF and CF@sub 2@ axial concentration profiles are hollow, showing that these species are produced at the reactor surfaces due to C@sub x@F@sub y@@super +@ ion bombardment, and are destroyed in the gas phase. The nature of the gas-phase destruction processes will be discussed, in relation to the formation of heavier C@sub x@F@sub y@ species. We also observed the occurrence of plasma instabilities over a wide range of gas pressure and injected RF power. This phenomena can mostly be explained in terms of relaxation oscillations between capacitive and inductive plasma modes as observed by previous workers in SF@sub 6@ plasmas, but with the added mechanism of the formation of heavy C@sub x@F@sub y@ oligomers, which are much more electronegative than the parent gas, CF@sub 4@.

#### 9:00am PS1-TuM3 Time-Resolved CF@sub 2@ Rotational Temperature Measurements in Inductively-Coupled Pulsed Plasmas, X. Wu, T.M. Bauer, University of New Mexico; J.L. Cecchi, University of New Mexico, US

We have measured the time evolution of the rotational temperature of CF@sub 2@ in pulsed plasmas. These measurements were performed in an inductively coupled plasma (ICP) reactor with a CHF@sub 3@/Ar gas mixture. 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 rotational temperature of CF@sub 2@ was determined from absorbance measurements, using a

wavelength-modulated diode laser spectroscopy system, modified to provide data with a time resolution of less than 0.1 ms. The @nu@1 band @super R@Q@sub 8@ of CF@sub 2@ eo<->oe and ee<->oo rotational lines J=16, 18, 19, 21-23 are used for analysis. >From the dependence of the line intensities on the energy of the lower state, we are able to extract the rotational temperature. Pulse frequency was varied from 4 to 20 Hz at duty factors from 10 to 50%. The CF@sub 2@ rotational temperature time evolution is characterized by a first order rise upon plasma ignition to a temperature that coincides with the steady state rotational temperature, providing the plasma-on time exceeds the heating time constant, which is typically in the range of 2-5 ms. Once the plasma is extinguished, rotational temperature shows first order decay to about 290  $\pm$  20K. The time constant for this decay is in the range of 5-10 ms.

9:20am PS1-TuM4 Measurements of H atom and CF@sub x@ Radical Densities in High-density CHF@sub 3@ Plasmas by Laser-induced Fluorescence, K. Sasaki, M. Okamoto, K. Kadota, Nagoya University, Japan CHF@sub 3@ plasmas are widely used for dry etching of SiO@sub 2@. There are many reports on the diagnostics of CF@sub x@ radicals in CHF@sub 3@ plasmas. However, reliable diagnostics of H atoms in CHE@sub 3@ plasmas have not ever been carried out. H atoms play an important role in scavenging F atoms which obstruct selective etching of SiO@sub 2@. In addition, excess H atoms may results in the damage of Si. Accordingly, the reliable diagnostics of H atoms in CHF@sub 3@ plasmas is an important issue. In the present work, we measured the absolute H atom density in high-density CHF@sub 3@ plasmas by (2+1)-photon laserinduced fluorescence spectroscopy.@footnote 1@ In addition, the absolute densities of CF and CF@sub 2@ radicals were also measured by laser-induced fluorescence. The experiments were carried out in a linear machine with a uniform magnetic field of 1 kG. Helicon-wave discharges were obtained by applying various rf powers to a helical antenna wound around a glass tube of 3 cm diameter. Since the plasma was confined radially by the external magnetic field, we had a slender plasma column with a diameter of 3 cm at the center of the cylindrical vacuum chamber. The H atom density was mainly on the order of 10@super 13@ cm@super -3@ at a CHF@sub 3@ gas pressure of 5 mTorr. The H atom density increased with the electron density of the plasma. Contrary to the H atom density, the CF@sub 2@ radical density was a decreasing function of the electron density. The H atom density was higher than the CF@sub 2@ radical density in plasmas with electron densities higher than 10@super 12@ cm@super -3@. The spatial distribution of the H atom density in lowdensity plasmas was roughly uniform, while in high-density plasmas, slightly hollow distributions (i.e., the H atom density in the plasma column was lower than that in the outside region) were observed in the H atom density. @FootnoteText@ @footnote 1@K. Sasaki, M. Nakamoto, and K. Kadota, Rev. Sci. Instrum., in press.

# 10:20am PS1-TuM7 c-C@sub 4@F@sub 8@/Ar Inductively Coupled Plasma Characterization, *M.T. Radtke*, *J.W. Coburn*, *D.B. Graves*, University of California, Berkeley

A study of the composition and structure of a c-C@sub 4@F@sub 8@/argon inductively coupled plasma is reported. In this study, we first measured discharge properties (plasma density, potential and electron energy distribution function) in a pure Ar discharge using a Langmuir probe. In subsequent experiments, small amounts of c-C@sub 4@F@sub 8@ were added to argon and the ion and neutral plasma composition was measured using separate quadrupole mass spectrometers. Neutral species number densities were measured using a calibrated, molecular beam sampled, appearance potential mass spectrometer. The dominant radicals were CF@sub 2@ and CF@sub 3@. Positive ions were measured in a separate mass spectrometer. The dominant positive ions were Ar@super +@, CF@super +@, CF@sub 2@@super +@, CF@sub 3@@super +@, C@sub 2@F@sub 4@@super +@, and C@sub 3@F@sub 5@@super +@. The neutral gas temperature was estimated using optical emission spectroscopy of the rotational temperature of trace N@sub 2@ in an argon discharge. Using the measurements, the total dissociation rate coefficients for c-C@sub 4@F@sub 8@ were estimated with a volume-averaged balance on c-C@sub 4@F@sub 8@ for each of the experimental conditions. From the measured EEDFs and the total dissociation rate coefficients, we tested a proposed total dissociation cross section. The proposed cross section was found to be consistent with the measured values to within the experimental uncertainty.

## **Tuesday Morning, October 30, 2001**

10:40am **PS1-TuM8 Use and Limitations of In-situ FTIR Spectroscopy for Fluorocarbon Plasma Analysis**, **B.A. Cruden**, M.V.V.S. Rao, Eloret Corp., NASA Ames Research Center; S.P. Sharma, M. Meyyappan, NASA Ames Research Center

Fourier Transform Infrared (FTIR) Absorption Spectroscopy has been used in an inductively coupled GEC Reference Cell for analysis of CF@sub 4@ plasmas. It was possible to detect undissociated CF@sub 4@ fraction and quartz window etch products (SiF@sub 4@, CO, COF@sub 2@) with this technique. From knowledge of the rotational/vibrational structure of the various bands, it is also possible to extract a gas rotational and vibrational temperature from this data. In interpretation of this data, many of the oftignored non-idealities of quanitative FTIR analysis are addressed. Of particular concern is the fact that Doppler-broadened absorption lines are significantly smaller than the instrument resolution. The resulting data represents a non-linear averaging of closely spaced absorbing lines. This produces cross-sections that do not obey Beer's law, i.e. are not constant. By examining the theory behind FTIR, these variations in cross-section are predicted for CF4. These theoretical errors are also manifested in inaccuracies in analyzing overlapping spectra. In FTIR, (as well as other absorption techniques) there is an additional averaging of absorption spectra over spatial coordinates. As a significant portion of the absorption signal will typically lie outside of the plasma, this averaging results in measurements that are not representative of the plasma species in terms of both number density and temperatures. When combined with the resolution limitations, it is predicted that a maximum measurable temperature exists that can differ significantly from the true plasma temperature. The results of a more carefully controlled absorption pathlength will also be presented.

#### 11:00am PS1-TuM9 Measurements and Models of Ion Energy Distributions in High-Density, Radio-Frequency-Biased CF@sub 4@/Ar Discharges, M.A. Sobolewski, Y. Wang, A.N. Goyette, National Institute of Standards and Technology

Ion dynamics in the narrow sheaths of high-density plasmas, especially in sheaths biased by radio-frequency (rf) voltages, are complicated and nonlinear. Models of such high-density, rf sheaths are needed to predict ion bombardment energies in simulations of high-density plasma etching. To provide data to test these models, we have measured ion energy distributions (IEDs) in CF@sub 4@/argon discharges in a high-density, inductively coupled plasma reactor, using a mass spectrometer equipped with an ion energy analyzer. Energy distributions of CF@super +@, CF@sub 2@@super +@, CF@sub 3@@super +@, and Ar@super +@ ions were measured as a function of pressure, mixture, inductive source power, rf bias frequency and rf bias amplitude. Simultaneous measurements by a capacitive probe and a Faraday cup provide enough information to completely determine the input parameters of sheath models and allow direct comparison of calculated and measured IEDs. For conditions where the rf bias period is much smaller than, or much larger than, the time it takes ions to cross the sheath, very simple models are able to predict the features of the measured IEDs. When the rf bias period approaches the ion transit time, however, more complicated models are required. One recently developed model@footnote 1@ which include a complete treatment of the time-dependent ion dynamics in the sheath, was found to accurately predict the behavior of measured IEDs over the entire range of rf bias frequency. @FootnoteText@ @footnote 1@M. A. Sobolewski, Phys. Rev. E 62, 8540 (2000).

#### 11:20am **PS1-TuM10 Submillimeter Absorption Spectroscopy of an Inductively Coupled Plasma**, *E.C. Benck*, *G. Golubiatnikov*, *G. Fraser*, National Institute of Standards and Technology

Millimeter and submillimeter (100 GHz to 1 THz) absorption spectroscopy is being developed as a sensor for measuring radical densities and temperatures in processing plasmas for microelectronics. Most molecules, radicals, and ions have transitions suitable for detection with submillimeter waves and the necessary spectroscopic data is available in the literature for determining the absolute radical densities. In addition, the narrow linewidths of cw submillimeter sources are suitable for measuring rotational, vibrational and translational temperatures of radicals. Initial measurements are being conducted with a backward wave oscillator (BWO) source and a liquid-He-cooled bolometer detector. Radical densities have been measured in an inductively coupled Gaseous Electronics Conference (GEC) RF Reference Reactor. At frequencies around 100 GHz, large absorption signals can be observed for CHF@sub 3@. Significant amounts of molecular dissociation can be measured when the discharge is ignited. The plasma does not significantly increase the translational temperature, probably due to a large volume of cool gas surrounding the

plasma. A 25 times increase in sensitivity would be expected for absorption measurements with frequencies around 500 GHz. Measurements of C@sub x@F@sub y@ and SiF@sub x@ radical densities will also be presented.

#### **Plasma Science**

Room 104 - Session PS2-TuM

#### **Emerging Applications of Plasmas**

**Moderator:** G.M.W. Kroesen, Eindhoven University of Technology, The Netherlands

#### 8:20am PS2-TuM1 Plasma Applications for Layer Transfer Technology, N.W. Cheung, University of California, Berkeley INVITED

Recent progress in bonding and thin-layer splitting enables a new approach to integrate dissimilar thin-film electronic materials. The transfer process incorporates the bonding of two substrates and the use of an ion-cut technique to separate thin films of semiconductors onto various receptor substrates. This paste-and-cut method is an appealing alternative to heterogeneous epitaxial growth approaches because each material layer for a given function can be grown/fabricated on an ideally suited substrate and then combined with a dissimilar receptor substrate. Plasma activated direct bonding and plasma implantation are two key process modules for the success of the layer transfer approach. We will present both lowtemperature bonding results using plasma surface activation and ion-cut results using plasma implantation. Material systems such as silicon-oninsulator, III-V semiconductors, and MEMS will be used as examples to illustrate versatility of this approach. Transfer of patterned materials and prefabricated devices have also been proven successful using this technique. \* Supported in part by the California SMART Program and National Science Foundation XYZ-on-a-Chip Program.

9:00am PS2-TuM3 High Density Discharges in Magnetic Fields: Examples of Plasma Thrusters and RF Ion Sources, A.B. Bouchoule, M. Irzyk, M. Prioul, GREMI Laboratory, Orléans University, France INVITED Magnetized plasmas are involved in various fields of research and applications for their ability to improve power deposition and reduce transport phenomena in gaseous discharges. Two illustrations are described in this contribution. The first one concerns plasma thrusters for space applications, based on the so-called "closed electron drift" discharges. The idea to use Eï,'B situations in order to achieve simultaneously a high ionization efficiency and an acceleration of the produced ions, at a level close to the discharge voltage, was initiated in the sixties. The improvements of these devices, and the present requirements for satellites control in space, lead to active R&D programs devoted to these thrusters. Their proved efficiency is already very high, but insights on their complex physics remains required, in order to improve modeling and simulations able to predict optimized designs. Obtained within the frame of a national program, results on time averaged or transient phenomena occurring in these thrusters will be described. From the experimental point of view, specific electrical and optical diagnostics have been developed and will be reviewed. In connection with modeling studies, these data improved our understanding of physical properties of these thrusters, both for their transient and time averaged behavior. The second one concerns high density ion sources, derived from RF inductive discharges in atomic or molecular gases, and using conventional gridded extraction system. Discharges have been obtained in various magnetic field configurations by using a "Nagoya type" external antenna. Results show the impact of the magnetic topography on efficiency and other characteristics of such ion sources. High atomic ion current densities have been obtained both for oxygen and nitrogen discharges. An extensive PIC simulation code for such high current density sources has been developed and will be presented, with its experimental validation.

#### 9:40am **PS2-TuM5 Characterization of Toroidal Plasma Sources for Semiconductor Processing Applications**, *T. Tanaka*, *C. Lai*, *M. Cox*, *T. Nowak*, *S. Wolff*, *S. Shamouilian*, *D. Silvetti*, *H. Hanawa*, Applied Materials Inc.

Toroidal plasma sources have been widely studied for nuclear fusion applications for several decades. The closed topography of the magnetic field provides a superior plasma confinement capability compared to other configurations. This is exemplified by the success of devices such as Tokamak. Over the last few years, there has been growing interest in the toroidal configuration for semiconductor processing applications. Because of the shape of the plasma, the source was primarily considered for downstream remote processing. In this context, plasma confinement is not

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as important due to the relatively high operating pressures typically used (100mTorr and above). The emphasis rather is placed on the ability to couple the inductive field much more effectively than with a conventional inductively coupled plasma (ICP) source while all but eliminating electrostatic coupling of RF power. Furthermore, by using a magnetic core to couple the driving inductive field, it is possible to operated these source at frequencies less than 400kHz. This is advantageous from the commercial stand point, because of the availability of inexpensive components for the power generator designed to operate at these lower frequencies. At Applied Materials, we have studied electrical properties of toroidal plasma sources. Experimental data is compared to a simple transformer model. We show that power coupling efficiency with these sources is extremely high. Coupling can exceed 98%, which is much higher than with a regular ICP. We also discuss some of the applications of these sources including CVD chamber cleaning

#### 10:00am **PS2-TuM6 Syntheses of Carbon Nanotubes and Nanocapsules by Plasma Chemical Vapor Deposition**, *Y. Hayashi*, *M. Kawana*, *S. Nishino*, Kyoto Institute of Technology, Japan

Carbon nano-materials such as nanotubes, fullerenes, or nanocapsules have been synthesized by the methods of arc discharge, laser evaporation, and thermal chemical-vapor-deposition (CVD). Recently it was reported that multi-wall carbon nanotubes were grown being well aligned perpendicularly to substrates of catalytic metals by plasma CVD, and they are expected to be used for a field emission display. From these results, we came to think that fine-particles of carbon nano-materials can be synthesized by glow-discharge plasma CVD. Fine-particles are suspended in a glow-discharge plasma for a long period because they are negatively charged in it. Therefore larger fine-particles composed of nano-materials can grow in the plasma. And also the modification and control of the materials are expected being suspended in a plasma. A surface-waveexcited 2.45GHz-microwave plasma was used for the syntheses. It was generated in a vacuum chamber by a microwave propagating through a slot antenna. A fine-particle collector, whose electric potential can be controlled from the outside, was put below the plasma. The gas of 10-40 % methane diluted in hydrogen was introduced into the chamber under a gas pressure of 100-700 Pa. Collected fine-particles were analyzed by scanning electron microscopy. Materials of tubular structure of 50-100 nm in diameter and cavity-like spherical and cubic structures of 100-200 nm in size were observed. They should be carbon nanotubes and nanocapsules. Detailed analyses by transmission electron microscopy are going to be performed.

#### 10:40am PS2-TuM8 The Development of the VASIMR Engine for Space Propulsion, J.P. Squire, F.R. Chang-Diaz, NASA, Johnson Space Center INVITED

The development of advanced propulsion technologies represents a cornerstone in the successful realization of long-term human space travel. Unlike their robotic precursors, human interplanetary spacecraft must be fast, reliable, "power rich," and be capable of reasonable abort options -essential features for the preservation of human life. The Variable Specific Impulse Magnetoplasma Rocket (VASIMR) is a new approach to plasma propulsion, which addresses these issues and provides an evolutionary path to fusion rockets, but with immediate and exciting non-fusion applications along the way. A NASA-led research effort, involving government, academia and private industry teams in the United States, is exploring the foundations of this concept, and pursuing its rapid development and test. This presentation will cover the basic principles of VASIMR operation, the latest experimental and theoretical results, as well as the most important technological developments and challenges for the future. Light gas (hydrogen, deuterium, helium and mixtures) helicon plasma production and subsequent Ion Cyclotron Resonant Acceleration (ICRA) are key experimental efforts. High density (~ 10@super 19@ m@super -3@) hydrogen, deuterium and helium plasma discharges have been achieved, with nearly 50% of the injected gas being accounted for in the plasma flow. Recent experiments with a strong magnetic choke (~ 1 tesla) downstream of the helicon source have demonstrated high Mach number (> 1) plasma flows. In certian conditions, high energy (> 50 eV) ion tails have been observed from the helicon source alone. Parametric (e.g. power, gas flow, and magnetic field) studies of the helicon source will be presented. ICRA experiments are in progress, so the configuration and most recent results will be discussed. The conceptual application of the VASIMR to fast human Mars missions, as well as plans for near-term flight demonstrations will also be highlighted.

11:40am **PS2-TuM11 Plasma Etching of Cesium Iodide@footnote 1@**, *X. Yang, J.A. Hopwood,* Northeastern University; *S. Tipnis, V. Nagarkar, V. Gaysinskiy,* Radiation Monitoring Devices, Inc.

Scintillator films that convert an incident x-ray image into visible light play an important role in many imaging applications. Because of its superior light output (59,000 photons/MeV), high density (4.54 g/cc), high effective atomic number (52) and rugged nature, CsI(TI) is often the material of choice for scintillator films. For adequate detection of 8-70 keV x-rays, 30-200 µm thick CsI films are needed. Spreading of light in the scintillator volume, however, limits the resolution of the resulting images. To address this problem we are micromachining CsI screens to form a finely pixelated structure. When coated with a low refractive index material, each micropixel acts as an optical waveguide that minimizes the spread of scintillation light in the screen. The micromachining process uses a high-density inductively coupled plasma to etch CsI samples held by a heated, rf-biased chuck. Fluorine-containing gases such as CF@sub 4@ are found to enhance the etch rate by an order of magnitude compared to Ar@super +@ sputtering alone. Without inert-gas ion bombardment, however, the fluorine-based etch becomes self-limited within a few microns of depth. The formation of a thick passivation layer on the sidewalls of etched features is confirmed by SEM. EDS indicates the passivation layer has a high ratio of Cs to I. Etching exhibits an Arrhenius-type behavior in which the etch rate increases from ~40 nm/min at 40 C to 380 nm/min at 330 C. This temperature dependence corresponds to an activation energy of 0.13 eV. Similar activation energies have been reported for the electronic sputtering of other alkali halides. This suggests that this CsI etch process, similar to alkali halide sputtering, is rate-limited by the thermal migration of ioninduced defects to the CsI surface. Additional results will support a more complete picture of the etching mechanisms. @FootnoteText@ @footnote 1@This work is supported by the NIH contract No. 2R44 CA76758-02.

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#### Plasma Science Room 103 - Session PS1-TuA

#### **Dielectric Etch I**

Moderator: M.J. Kushner, University of Illinois, Urbana

2:00pm PS1-TuA1 Gas Phase and Surface Diagnostic Measurements of High-density Plasma-based Etching Processes for Dielectrics Based on C@sub 4@F@sub 8@ Gas Mixtures with Ar, O@sub 2@ and N@sub 2@, X. Li, University of Maryland; M. Fukasawa, Sony Corporation, Japan; G.S. Oehrlein, University of Maryland; M. Barela, University of New Mexico, U.S.; H.M. Anderson, University of New Mexico

High-density plasma etching of dielectric films, e.g. SiO2 and low dielectric constant films, is an important process steps in integrated circuit manufacturing. Etching selectivity relative to the etching mask and insulating etch stop materials is required for these processes. Frequently gas mixtures rather than pure fluorocarbon gases are being employed. In this work we have studied the effect of adding O2 and Ar, two important gas additives, to C4F8 discharges produced using an inductively coupled plasma source. We measured fluorocarbon deposition and etching rates, SiO2, resist and silicon etching rates as a function of gas composition. In parallel, the absolute partial pressures of CF2, CF and COF2 radicals were measured using infrared laser absorption spectroscopy. Mass spectrometry was used to establish the importance of other gas phase species. In-situ ellipsometry and x-ray photoemission spectroscopy were used to obtain information on the surface processes for the various thin film materials. The effect of admixing O2 or Ar is shown to produce dramatic and nonobvious changes in the gas phase and surface chemistry, and enables to better address the technological objectives of the etching process. For instance, we have observed that the SiO2/resist and SiO2/Si etching selectivity can be increased by more than a factor of 3x at 20 mTorr by adding about 50% of Ar to C4F8. The infrared absorption measurements show that the partial pressures of CF and CF2 are increased by the addition of Ar despite the lower partial pressure of C4F8, and thicker fluorocarbon surface reaction layers are produced on silicon surfaces during steady-state etching.

#### 2:40pm PS1-TuA3 A 0.09µm-capable Plasma Etching of Dielectrics and its Reaction Mechanism, S. Tachi, Hitachi, Ltd., Japan; J. Ghormley, Hitachi America Ltd. INVITED

For a well-controlled dielectric etching with 0.18-0.13µm capability, a considerable amount of molecular species, CF@sub 2@, has been needed in conjunction with an intentionally suppressed fluorine, F, in (C@sub 4@F@sub 8@/C@sub x@F@sub y@+Ar) plasma, and, at the same time, having a sufficient ion-flux. Multi-dissociative collision phenomenon and multiple gas fragmentation should be avoided in gas phase for this purpose. For designing such plasma, chamber geometry, and processes, further evolution seems to be necessary. In this paper, a highly selective contact etching against the photo-resist mask over the whole wafer, and a relatively high oxide etch rate with good reproducibility are discussed in terms of a new planer-type, high-medium density plasma, having a doubled-near-surface structure, and experimenting with a noble processing with a computationally feed-forwarded architecture.

#### 3:20pm PS1-TuA5 Plasma Etching Chemistry and Kinetics for Silicon Oxide Thin Films, O. Kwon, H.H. Sawin, Massachusetts Institute of Technology

Surface kinetics study of silicon oxide etching with fluorocarbons in inductively coupled plasmas High density fluorocarbon plasma for silicon oxide etching has various ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity of photoresit. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as functions of ion bombardment energy, ion impinging angle, ion-toneutral flux ration, which are necessary for profile evolution modeling of silicon oxide etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to differentially pumped side chambers. Surface reaction is studied by measuring etching and deposition rate with quartz crystal microbalance(QCM). At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. Etching or deposition rate is measured with QCM as functions of ion acceleration energy, ion impinging angle, ion-to-neutral flux ration with various fluorocarbon plasmas. With florocarbon plasma with deposition chemistry, fluorocarbon deposition was observed at low ion energy, high

ion impinging angle, low plasma power and high pressure. A model describing both deposition and etching regimes is suggested.

#### 3:40pm **PS1-TuA6 Oxide Etch Behavior in an Inductively Coupled C@sub 4@F@sub 8@ Discharge Characterized by Diode Laser Spectroscopy**, *H.M. Anderson*, University of New Mexico; *M. Barela*, University of New Mexico, U.S.; *G. Courtin*, University of New Mexico; *K.S. Waters*, Intel

An inductively coupled GEC Reference Cell has been modified to allow etching of oxide wafers under conditions typical of commercial high density plasma reactors. This study reports on the oxide and photoresist etch characteristics as a function of reactor source power, bias power and pressure. Diode laser absorption spectroscopy (DLAS), OES and Langmuir probe measurements were made at the same time. DLAS has shown that C@sub 4@F@sub 8@ is largely dissociated to form C@sub 2@F@sub 4@, CF@sub 2@ and CF in the discharge. Over an oxide surface, CF@sub 2@ and CF are consumed in the oxide etch process, but only when the bias power is sufficient to keep the oxide surface clean through energetic ion bombardment. Langmuir probe measurement of the ion current density was used to estimate the bias voltage at the wafer at which this transition took place. For C@sub 4@F@sub 8@, this transition occurs at ~ 60 eV (75 W bias power) in the GEC Cell. At higher bias powers (125 W) where oxide etching is fast (~600 nm/min.), CF@sub 2@ appears to be the key radical for the etch process since ~50 percent (2.7-3.0 mTorr in a 15 mTorr C@sub 4@F@sub 8@ discharge) is consumed. These values were obtained by comparing the CF@sub 2@ concentrations over non-reactive wafer surfaces versus blanket oxide wafer surfaces undergoing etching. CF is shown to display a similar trend, but its concentration is an order of magnitude less than CF@sub 2@, and consequently cannot account on a mass basis for the amount of reactants necessary to balance the amount of etch products. Over a PR surface, neither CF@sub 2@ nor CF concentrations vary as a function of PR etch rate. Consequently, they do not appear to be involved in the PR etch mechanism. However, PR etching is also critically dependent on bias power. PR films etch presumably due to energetic ion bombardment that degrades the PR film, making it liable to attack by fluorine. This project was funded by SEMATECH and NSF

#### 4:20pm **PS1-TuA8 Characterization of Hydrofluorocarbon Reactants for Selective Silicon Nitride Plasma Etch Applications**, *E.A. Hudson*, *H. Zhu*, *D. Pirkle*, *J. Luque*, Lam Research Corp.; *J.P. Booth*, Ecole Polytechnique, France

Certain dielectric etch applications require the removal of silicon nitride films with high selectivity to silicon dioxide. An important example is found in dual-damascene integration schemes using organic low-k dielectric materials and nitride diffusion barriers. At the completion of the via etch, the nitride at the via bottom must be removed without penetrating the oxide hardmask which protects the top surface of the low-k dielectric film. Nitride-to-oxide etch rate selectivities of >10:1 are desirable. To understand how this selectivity may be achieved, and to compare the effects of different hydrofluorocarbon feed gases, a series of processes have been evaluated using a dual-frequency, capacitively-coupled, dielectric etch system. The feed gases for the processes are Ar and O@sub 2@, combined with a hydrofluorocarbon from the series CH@sub x@F@sub y@, where x ranges from 0 to 4, and y=4-x. Selectivity trends were determined from blanket nitride and oxide etch rates. Trends in the plasma chemistry were characterized using broad-band UV absorption spectroscopy. CF, CF@sub 2@, and CH@sub 3@ densities were measured using absorption bands in the 200-270nm range. This method directly measures absolute densities of ground state radicals in the plasma. Best selectivity results were obtained using CH@sub 3@F, which produced selectivities >20:1 for blanket films and for patterned wafers. The CF@sub 2@ density was found to be relatively high for processes using CHF@sub 3@, and very low for processes using CH@sub 3@F. In contrast, the CF density followed a more linear trend through the hydrofluorocarbon series. Also the production of CH@sub 3@ radical from CH@sub 3@F reactant was much less than from CH@sub 4@ reactant, suggesting that the direct removal of atomic F from CH@sub 3@F is not a favorable dissociation pathway. These results and others are interpreted to understand the mechanism for high nitride-to-oxide selectivity.

4:40pm PS1-TuA9 Modeling of SiO@sub 2@ Feature Etching in Fluorocarbon Plasmas: The Effect of Gas Phase Composition on Aspect Ratio Dependent Phenomena, G. Kokkoris, E. Gogolides, National Center for Scientific Research (NCSR) "Demokritos", Greece; A.G. Boudouvis, National Technical University of Athens (NTUA), Greece

There are several problems during etching of SiO@sub 2@ features in fluorocarbon plasmas such as Reactive Ion Etching lag (RIE lag), inverse RIE

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lag,@footnote 1@ and etch stop,@footnote 2@ which have been observed to depend on Aspect Ratio (AR) of the etched feature@footnote 3@ and are included in the general term Aspect Ratio Dependent Etching (ARDE). A goal to achieve in feature etching is Aspect Ratio Independent Etching (ARIE). The context of this work involves modeling of the effect of gas phase composition on AR dependent phenomena during SiO@sub 2@ feature etching in fluorocarbon plasmas. The effort to accomplish this task requires: a) A predictive surface model@footnote 4@ for open area SiO@sub 2@ etching; the surface "coverage", @theta@, is assigned to all species (fluorine atoms, fluorocarbon radicals, and a surface polymer) in the mixed layer created under ion bombardment. The "polymer surface coverage", @theta@@sub P@, could be thought of in a more general sense as a normalized thickness of the polymer overlayer. The model coefficients have been calculated@footnote 4@ by fits to beam experiments' results. b) A model to calculate the local values of neutral and ion fluxes (flux calculator@footnote 5@) inside etched features, which takes into account shadowing of neutral and ion flux and re-emission of neutral flux. Charging effects are not explicitly considered at present. c) A coupling of model (a) with (b) to calculate the local etching rate inside features. The focal point of the coupling is the simultaneous@footnote 5@ calculation of local fluxes and effective sticking coefficients of the neutral species at each elementary surface of the structure being etched. The goal of this work is the prediction of several phenomena (RIE lag, inverse RIE lag, etch stop, and ARIE) and their relation with gas phase composition. A new approach is presented based on maps of two types. The maps of the first type show the effect of gas phase composition on etching yield at the bottom of an etched feature. In the second type of maps the effect of gas phase composition on ARDE and ARIE is illustrated. Gas phase composition is divided into regions characterized by the observation of a specific phenomenon in each region (e.g. RIE lag, inverse RIE lag, ARIE). Furthermore, a preliminary investigation of processes windows satisfying specific demands on ARIE, etching rate magnitude, and etching rate (SiO@sub 2@/Si) selectivity is done. @FootnoteText@ @footnote 1@ M. F. Doemling, N. R. Rueger, and G. S. Oehrlein, Appl. Phys. Lett. 68, 10 (1996). @footnote 2@ O. Joubert, G. S. Oehrlein, and Y. Zhang, J. Vac. Sci. Technol. A 12, 658 (1994). @footnote 3@ R. A. Gottscho, C. W. Jurgensen, and D. J. Vitkavage, J. Vac. Sci. Technol. B 10, 2133 (1992). @footnote 4@ E. Gogolides, P. Vauvert, G. Kokkoris, G. Turban, and A. G. Boudouvis, J. Appl. Phys. 88, 5570 (2000). @footnote 5@ G. Kokkoris, E. Gogolides, A. G. Boudouvis, Etching of SiO@sub 2@ and Si features in fluorocarbon plasmas I: Effect of gas phase composition on aspect ratio dependent phenomena in trenches, submitted for publication to Journal of Applied Physics.

## 5:00pm **PS1-TuA10** Inductively Coupled Plasma Etching for Arrayed Waveguide Grating Fabrication in Silica on Silicon Technology, S. Bretoiu, D. Di Mola, E. Fioravanti, S. Visona, Agilent Italy

Arrayed Waveguide Gratings (AWGs) in silica on silicon technology were fabricated and tested in our laboratory. The silica optical layers were all deposited in LPCVD furnaces, and waveguide core was etched using a photoresist mask in an inductively coupled plasma source with C@sub 4@F@sub 8@/O@sub 2@/He gas mixture. This article reports the dependence of important process parameters, included aspect ratio dependent etch rate (A.R.D.E.) effect, selectivity and waveguide side wall angle, on RF power, chamber pressure and gas flow rates. In particular the effects of He and O@sub 2@ addition on A.R.D.E. effect and waveguide side wall angle were investigated. Based on these results a reliable and high throughput process was set up to etch silica waveguides suitable for AWG fabrication, with etch rate higher than 300 nm/min, selectivity on photoresist higher than 5:1 and waveguide side wall angle higher than 88.5°. Measurements of first 16 Channel 200 GHz AWGs fabricated with this process are presented and discussed. To conclude preliminary results are reported about etching of high aspect ratio (>3:1) trenches with depths greater than 15  $\mu$ m, to be used for stress releasing grooves in AWGs.

#### **Plasma Science**

Room 104 - Session PS2+TF+SE-TuA

#### PECVD/IPVD

Moderator: A.B. Bouchoule, University d'Orleans, France

2:00pm PS2+TF+SE-TuA1 Mechanisms Involved in the PECVD of Thin Films in Low Pressure Organosilicon Plasmas, A. Granier, A. Goullet, K Aumaille, G. Borvon, Institut des Matériaux Jean Rouxel, France; C. Vallee, LEMD, France; G. Turban, Institut des Matériaux Jean Rouxel, France INVITED Low pressure organosilicon plasmas are widely used for the deposition of thin organic and inorganic films, used for their dielectric, optical and barrier properties. The organosilicon precursors such as tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO) or tetramethylsilane (TMS) are used either pure or mixed with Ar, He, O@sub 2@ or N@sub 2@. The subject of this talk is to present the state of knowledge on the mechanisms involved in the low pressure (1 to 50 mTorr) organosilicon plasmas namely, both homogeneous and heterogeneous reactions. Since the data related to organosilicon reactions are relatively poor, information has to be deduced from experiments. Systematic plasma analyses have been carried out in low pressure RF inductively coupled TEOS and HMDSO based plasma by optical emission spectroscopy, Langmuir probes and mass spectrometry coupled with real time monitoring of the film growth by ellipsometry. It is deduced that electrons are more efficient than O atoms to break HMDSO and TEOS molecules. Organosilicon dissociation rates higher than 90% are easily reached. It is likely that the by-products of the electron impact dissociation are light H and CH@sub 3@ radicals and big fragments directly issued from the organosilicon molecule. On the other hand, in order to get better insight in heterogeneous reactions with O, H atoms, organosilicon film have been exposed to pure Ar, oxygen and hydrogen plasmas. It is demonstrated that oxygen atoms are very efficient to oxidize the organic part of the films, and that a 50 nm thick organosilicon film can be totally transformed into a porous silica film, upon exposition to an oxygen plasma.

#### 2:40pm PS2+TF+SE-TuA3 Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition (ECR-PECVD) of ZrO@sub 2@ on Silicon, B.O. Cho, J. Wang, S.X. Lao, J.P. Chang, University of California, Los Angeles

ZrO@sub 2@ is one of the most promising high dielectric constant (k) materials to replace SiO@sub 2@ in ultra large scale integration chip fabrication because of its wide band gap and low leakage current level. We developed an ECR-PECVD process to deposit ZrO@sub 2@ with zirconium tetra-tert-butoxide (Zr(OC@sub 4@H@sub 9@)@sub 4@) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O@sub 2@ as an oxidant. Quadrupole mass spectroscopy, optical emission spectroscopy (OES), and Langmuir probe were used to characterize the plasma. The mechanisms of precursor decomposition and oxidation reactions including Zr-ligand bond dissociation and ZrO formation were investigated by analyzing the radical appearance potentials. The decomposition and oxidation reactions in the plasma were mainly controlled by the flow rate ratio of O@sub 2@ to Ar (O@sub 2@/Ar), varving between 0 and 10, and the electron temperature of 2-8 eV with the typical value of 3-4 eV. The OES intensity ratio of C@sub 2@ at 516.52 nm to O at 777.42 nm linearly scaled with the incorporated carbon concentration in the deposited film, which were determined by x-ray photoelectron spectroscopy and secondary ion mass spectroscopy. Since carbon incorporation greatly influenced the electrical performance of the film, low carbon-content, stoichiometric, and amorphous ZrO@sub 2@ was obtained at O@sub 2@/Ar>1 without substrate heating. We also deposited the film at elevated substrate temperatures around 400 °C with the controlled substrate bias to obtain carbon-free amorphous ZrO@sub 2@. The as-deposited ZrO@sub 2@ film between Al electrode and Si in capacitor devices showed good capacitance-voltage and current-voltage characteristics, which yielded k=22 and J=4x10@super -5@A/cm@super 2@ at -1.5 V, respectively. Scanning electron micrograph (SEM) showed that highly conformal film deposition could be achieved over 300 nm diameter cylindrical memory structure with an aspect ratio of 4.

3:00pm PS2+TF+SE-TuA4 Deposition of a-C:H Films: Plasma Chemistry and Material Properties, J. Benedikt, Eindhoven University of Technology, The Netherlands; K.G.Y. Letourneur, Eindhoven University of Technology, The Netherlands, Netherlands; M. Wisse, Free University, The Netherlands; D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

Remote Ar-C@sub 2@H@sub 2@ plasma created by means of a cascaded arc is used for fast rate deposition of hard hydrogenated amorphous

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carbon films (a-C:H, rate up to 50 nm/s, hardness up to 14 GPa). First the densities of the radicals have been investigated in detail using cavity ring down absorption spectroscopy (CRDS). C@sub 2@, CH, C and H radicals were spectroscopically identified and measured as a function of C@sub 2@H@sub 2@ gas flow admixture. C@sub 2@H radical is still not spectrally resolved but broad band absorption observed around 250, 276 and 431 nm can be ascribed to this radical. The main mechanism of the dissociation of acetylene and other radicals in the plasma is a charge exchange reaction with argon ion and subsequent dissociative recombination of the molecular ion with an electron. Thus the composition of the plasma depends strongly on the amount of argon ions (and electrons) available in comparison with the amount of acetylene molecules injected. A plug-down model of plasma chemistry was made to simulate measured densities and to find creation channels of the different radicals. Second in-situ real time ellipsometry was used during deposition to measure the refractive index and the growth rate of the films. Clear correlation between plasma composition and the properties of the film was observed. Both the refractive index (which is in our case correlated with hardness) and the growth rate increase with increasing acetylene flow. The highest values are reached when the acetylene flow into the chamber is equal or higher than the argon ion flow emanating from the plasma source. In this case the C@sub 2@H radical is dominantly present in the plasma and is the main growth precursor of our films

3:20pm **PS2+TF+SE-TuA5 Study of SiO@sub x@N@sub y@ Films Deposited by Radio-Frequency Plasma Assisted Electron Cyclotron Resonance**, *J.D. Brewer*<sup>1</sup>, University of North Carolina at Chapel Hill; *A. Raveh*, NRCN Division of Chemistry, Israel; *E.A. Irene*, University of North Carolina at Chapel Hill

New techniques for the development of higher dielectric constant materials as a passivation layer of silicon remains a challenge. To this end, a radio-frequency (RF) plasma process, in combination with an electron cyclotron resonance (ECR) plasma, was employed at low pressures (100-1000 mTorr) and low substrate temperatures (100-300°C) to grow silicon oxynitride thin films on p-type Si (100) wafers. N@sub 2@ and O@sub 2@ were used as gas sources to allow separate control of the amount of N and O ions and radicals, thus affording control of film stoichiometry. Films were produced with an ECR power of 300 W and an RF bias range of 0 to -80 V. The ability to tailor film properties such as; composition, interface states, morphology and structure was made possible by varying plasma processing parameters. Spectroscopic ellipsometry, atomic force microscopy, Auger electron spectroscopy, x-ray photoelectron spectroscopy and capacitancevoltage measurements were performed on the silicon oxynitride layers. The nitrogen to oxygen ratio in the silicon oxynitride films was found to depend on competitive processes between N@super +@ and O@super -@ species. Less negative voltages (> -20 V) produced a greater content of oxide due to a larger concentration of O@super -@ ions, while more negative voltages (< -50 V) produced NO and N@super +@ ions and radicals forming a greater content of nitride in the films. In addition, the effects of pressure, flow-rate ratio, time, temperature and ECR power on the fabricated film properties will be presented.

4:20pm PS2+TF+SE-TuA8 An In Situ Study of the Interactions of Atomic Deuterium with Hydrogenated Amorphous Silicon Thin Films Using Multiple Total Reflection Fourier Transform Infrared Spectroscopy, S. Agarwal, University of California, Santa Barbara; A. Takano, Fuji Electric Corporate Research and Development, Ltd., Japan; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands; D. Maroudas, E.S. Aydil, University of California, Santa Barbara

Atomic hydrogen plays a crucial role in the deposition of amorphous hydrogenated silicon (a-Si:H) from silane containing discharges which are often diluted with hydrogen. However, during the deposition process the role of atomic hydrogen cannot be isolated from the other radicals impinging onto the surface. In order to isolate the effect of H atoms, as deposited a-Si:H films were exposed to a deuterium plasma and subsequent compositional and structural changes in the film were studied using in situ multiple total reflection Fourier transform infrared (MTR-FTIR) spectroscopy. The use of atomic deuterium generated by the plasma allowed us to observe both the abstraction-passivation reaction and the insertion reaction since the stretching modes of SiH@sub x@ (x = 1,2,3) appear at different wavenumbers. a-Si:H thin films were deposited in an inductively coupled plasma reactor at 200 °C. The deposited films were exposed to a series of one second deuterium plasma pulses at different substrate temperatures. In situ MTR-FTIR was

used to observe the changes in the film after each pulse. Peak assignments were made and the IR data was deconvoluted for both the SiH@sub x@ and SiD@sub x@ part of the spectrum. Removal of surface hydrides is very fast and there is no activation barrier for the abstraction-passivation reaction in agreement with atomistic calculations of this barrier. The modification of the bulk film through abstraction and insertion reactions is limited by diffusion of D. Moreover, we find evidence for the presence of a thin sub-surface region (<30 Å) that has a higher concentration of silicon diand trihydrides and strained silicon-silicon bonds. Insertion into the Si-SiH@sub2@ bonds in this layer is faster than insertion into Si-SiH.

#### 4:40pm PS2+TF+SE-TuA9 A New and Fast In-situ Spectroscopic Infrared Absorption Measurement Technique for Submonolayer Detection at High Growth Rate, *M.F.A.M. van Hest*, *A. Klaver, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Silicon oxide like films are deposited at high rate (up to 200 nm/s) using an expanding thermal plasma (Cascaded arc) in combination with hexamethyldisiloxane (HMDSO) and oxygen as deposition precursors. In general Fourier transform infrared (FTIR) reflection spectroscopy is a useful tool for in situ analysis of the film deposition growth process. However this technique is difficult to apply when the film deposition rate is reaching high values (10 to 100 nm/s). When studying submonolayer growth, the time resolution of a FTIR setup is too long (typical 0.1 - 1 s). So another technique has to be used to improve the time resolution. The heart of the new technique is a grating mounted on a laser scanner, which oscillates at a frequency of up to 300 Hz. Only a small part of the infrared spectrum will reach the detector (MCT). The rotation angle is limited and therefore the spectral bandwidth with respect to a FTIR spectroscope is small (200 cm@super -1@ at 1000 cm@super -1@), but the time resolution improved (1.7 to 10 ms). A cascaded arc is used as a light source, because if its high radiation temperature it produces more infrared light than a glowbar. To make submonolayer absorption detectable, single reflection is not sufficient; therefore attenuated total reflection (ATR) crystals are used as substrates. These crystals make multiple (50) interactions of the infrared beam with the depositing film possible, leading to a higher measured absorption. The set up will be presented in detail as well as the first results of the in situ study of the film growth of silicon oxide like films. Together with the in situ study also a plasma post treatment study has been performed. With this the resistance of the deposited films towards an argon/oxygen plasma has been studied. This study shows that the deposited films contain a significant amount of carbon, which can be removed by post treatment.

#### 5:00pm PS2+TF+SE-TuA10 Reaction Mechanism of PECVD to Produce Low Dielectric Constant Thin Films, Y. Shimogaki, University of Tokyo, Japan INVITED

Ever growing device integration now requires low dielectric constant materials for inter metal dielectrics to improve speed performance of ULSIs. SiO:F (fluorinated silicon oxide) and a-C:F (amorphous fluoro carbon) films produced by PECVD are the major candidates for this purpose. In case of SiO:F film deposition from SiH@sub 4@/N@sub 2@O/CF@sub 4@, we found that fluorine addition to SiO@sub 2@ reduces Si-OH bonds which are the major dielectric component in SiO@sub 2@ films by PECVD. Fluorine addition also reduces growth rate and improved step coverage. We have examined the gas flow rate dependency of the growth rate by keeping the other process parameters constant. The growth rate of SiO:F film increased and the step coverage profile became poor by increasing gas flow rate. We have extracted suitable reaction kinetics to explain these phenomena. The reaction mechanism, which contains two major species in film deposition, obtained from this experimental approach well explained the step coverage behavior. In case of a-C:F film deposition from C@sub 2@F@sub 4@, the film growth rate decreased by increasing the gas flow rate. This is due to the gas phase reactions that produce main film precursors, like as CE@sub 3@@sup +@ ion and CE@sub 2@ radical. We also evaluated the contribution of ionic species and neutral radical species using step coverage into micron scale features. We found that radical species contributes to have uniform step coverage, but most of the film forming species are ionic ones and they contribute to make thermally stable films.

#### Plasma Science Room 134/135 - Session PS-TuP

#### Plasma Deposition, Modeling, and Emerging Applications Poster Session

#### PS-TuP1 A Comparitive Study of PECVD of Fluorocarbon Films Using C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ Precursors, I.T. Martin, G. Malkov, E.R. Fisher, Colorado State University

Plasma polymerization of fluorocarbons has been studied extensively. Recently, greater control over film characteristics has been attained through manipulation of plasma parameters, such as the formation of highly ordered CF@sub 2@ rich films using downstream continuous wave (CW) and pulsed hexafluoropropylene oxide (HFPO) plasmas. Here, we explore films deposited from the fluorocarbon precursors, octafluoropropane (C@sub 3@F@sub 8@) and octafluorocyclobutane (C@sub 4@F@sub 8@). These compounds are used industrially as alternatives to CF@sub 4@ and C@sub 2@F@sub 6@ in PECVD chamber cleans. Here, we characterize film properties as a function of input power, distance from the glow, and pulsed vs. CW conditions. Data from FTIR and XPS show films deposited with downstream CW and pulsed plasma conditions have higher CF@sub 2@ content and lower cross-linking with both precursors. However, films deposited with C@sub 4@F@sub 8@ plasmas have a lower mechanical flexibility than those deposited with C@sub 3@F@sub 8@ plasmas. Comparison to the HFPO system suggests the oxygen present in the HFPO system may be integral to the deposition of highly ordered films. In addition to film characterization, we have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF@sub 2@ radicals during plasma processing. CF@sub 2@ surface loss coefficients determined for 5-150 W C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas indicate relatively high levels of scattering in these systems (S>1). Scatter values greater than unity indicate CF@sub 2@ radicals are produced at the surface. Substrate biasing and ion removal techniques will be used to determine the effects of ions on these measurements. These data can be correlated with mass spectral data collected with the IRIS apparatus. Collectively, the data presented provide a comprehensive picture of these fluorocarbon systems, from the gas-phase to the material to the plasma-surface interface.

**PS-TuP2** Spectroscopic Study of the Energetic Character of O@sub 2@/Ar/Tetramethyltin Discharge used for the Deposition of Transparent Conductive Tin Oxide Thin Films, *F. Arefi-Khonsari*, ENSCP-University of P.&M.Curie-Paris-France; *N. Bauduin*, ENSCP-University of P.&M.Curie-Paris-France, France; *J. Amouroux*, ENSCP-University of P.&M.Curie-Paris-France

Non stoichiometric tin oxide thin films have been deposited from an O@sub2@/Ar/tetramethyltin (TMT) mixture in a RF glow discharge parallel plate reactor at low pressure (15 Pa) and at low temperature (25-80 °C). The spectroscopic study of the discharge was performed with the help of optical emission spectroscopy and mass spectrometry. The aim of this work was to determine the role of the experimental parameters on the energetic and chemical characteristics of the discharge. This work was carried out by determining the vibrational temperature of N2 (C@sub 3@@PI@@sub u@,v'-B@sub 3@@PI@@sub g@,v" transition) as well as the rotational temperatures of OH (Q@sub 2@ rotational branch of the A@sub 2@@SIGMA@@super +@,v'=0 - X@sub 2@@PI@@sub i@,v'=0 transition) and N@sub 2@@super +@ (R0 rotational branch of the B@sub 2@@SIGMA@@sub u@@super +@, v'=0 - X@sub 2@@SIGMA@@sub g@@super +@,v'=0 transition). The mean electronic temperature was determined with the help of OES, by using Junk and Getty's model. In the latter they have used a maxwellian distribution of the EEDF which cannot hold in our conditions. That is why we have used the nonmaxwellian distribution of the energy of the electrons by solving the Boltzman's equation. The results show that the energetic character of the discharge was not modified when the organometallic precursor (i.e. TMT) was introduced. The dissociation rate increased with the power giving rise to a plateau around 200 watts which corresponded to the conditions where carbon free SnO@sub 2@ films were deposited. As for the biasing of the substrate electrode, which gave rise to an increase of the conductivity from 0.01 to 100 @ohm@@super -1@.cm@super -1@ with a decrease of the gap energy (from 3.5 to 2.5 eV), it did not give rise to a change of the energetic character. However, a spatially resolved study of the discharge by

OES showed an increase of the intensities in the sheaths of both electrodes.

PS-TuP3 Spatial and Temporal Behaviour of the Plasma Parameters in a Pulsed Magnetron Discharge, J.T. Gudmundsson, University of Iceland, Iceland; J. Alami, U. Helmersson, Linkoping University, Sweden

We demonstrate the evolution of the electron energy distribution and the plasma parameters in a high density plasma in a pulsed magnetron discharge. The high density plasma is created by applying a high power pulse (1 -- 3 MW) with repetition frequency 50 Hz to a planar magnetron discharge. The spatial and the temporal behaviour of the plasma parameters are investigated using a Langmuir probe; the electron energy distribution function, the electron density and the average electron energy. Furthermore we report on the variation of the plasma parameters and electron energy distribution function with pulse length and the gas pressure in the pressure range 0.5 -- 5 mTorr. The electron density in the vicinity of the substrate, 20 cm below the cathode target, peaks at roughly 1 x 10@super 18@ m@super -3@ at 2 mTorr in a pulsed discharge with average power 300 W. Towards the end of the pulse two energy groups of electrons are present with a corresponding peak in average electron energy. With the disapperance of the high energy electron group the electron density peaks and the electron energy distribution appear to be Maxwellian like. Following the electron density peak the plasma becomes more Druyvesteyn like with higher average electron energy.

PS-TuP4 Evaluation and Measurement of Ionization Fraction in Ionized Physical Vapor Deposition using Parallel-plates Method, K.-F. Chiu, National Tsing Hua University, Taiwan; Z.H. Barber, University of Cambridge, UK; R.E. Somekh, Plasmon Data Systems Ltd., UK

The ionization fraction of the depositing flux of the ionized physical vapor deposition (IPVD) process was measured using a parallel-plates method. The method uses two parallel stainless steel plates forming a  $1^2$  mm slot, and measures the ionization fraction of the depositing flux travelling through the slot. A simple one-directional electric field was applied by biasing one side of the plates with the other side earthed. Negative bias was applied to avoid serious purperbation of the plasma. Since the ionized atoms are attractive to the biased side, the ionization fraction can be obtained by comparing the deposition rates with and without bias. This method was evaluated by modelling the trajectories of the depositing ions under the influence of the applied electric field.

# PS-TuP5 ICP Source Designs with Azimuthal Field Symmetry Despite a Current Node, S. Srinivasan, L.J. Overzet, M. Goeckner, University of Texas at Dallas

Inductively coupled plasma source-coils can be modeled as transmission lines. The current characteristics across the transmission line are dependent on the terminating impedance and the constitutive parameters of the source. When the terminating impedance of the planar coil is different from the characteristic impedance, it results in standing waves. When the size of the planar coil exceeds one-quarter wavelength, the standing waves can produce a current node on the source coil. The location of the current node along the source coil is dependent on the frequency of operation and terminating impedance. These current nodes and the formation of standing waves along the source coil induce azimuthal asymmetry in the electric fields and bring about non-uniform power deposition in the plasma. We can change the geometry of the coil by making it three-dimensional with the adjacent loops of the source running in opposite directions to reduce azimuthal asymmetry and minimize the effect of a current node. The position of the current node along the three dimensional source affects the symmetry of the electric fields. The exact relationship between the field asymmetry and the position of the current node is being investigated. The field variations can be minimized by placing the current node on a loop that is pushed away from the dielectric window. The length of the three-dimensional source can also be adjusted to yield uniform fields and power deposition in the plasma. A three-dimensional source coil geometry can allow sufficient latitude for designing the direction in which the currents travel and to specify how far the different loops need to be from the dielectric window. We believe that the isolation of the node loop in the source is a key to obtaining azimuthal symmetry. Increasing the size of the source even to include multiple nodes would not be an issue then. This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 009741-0081-1999.

**PS-TuP6 Control of Dissociation by Different Dilution Gases for Plasma Processing**, *KJ Taylor*, University of California, San Diego; *S.M. Yun*, Lam Research Corporation; *Y.J. Park*, Samsung Electronics Corporation; *G.R. Tynan*, University of California, San Diego

Electron temperature and electron density are modeled by using simple 0d particle and power balance modeling and measured by Langmuir probe in pure He, Ar, and Xe plasmas. Trace amounts of oxygen gas is added to each of the inert gas plasma and dissociation of oxygen gas is studied by actinometry and by mass spectroscopy with various powers and various ratios of O2/inert gas. Reasonable agreement between these results and the neutral atomic oxygen density estimated using a simple model based on the measured electron density and temperature. Preliminary dissociation results using fluorocarbon will also be shown.

PS-TuP7 Comparative Study of N@sub 2@/CH@sub 4@ Plasmas in Active Discharges and in Flowing Afterglow Conditions, *R. Hrach*, Charles University, Czech Republic; *J.C. Legrand, A.M. Diamy*, Universite Pierre et Marie Curie, France; *V. Hrachova, M. Vicher*, Charles University, Czech Republic

Methane is widely used in plasma processing. Experimental techniques used for the decomposition of methane into simpler hydrocarbons can be divided into two groups - processing in active discharges and processing in flowing afterglow conditions. While the first group of discharges can lead to preparation of solid products, the lower energies in afterglows are much more convenient for efficient gaseous chemistry. The aim of this contribution is to give an insight into the basic mechanisms leading to decomposition of methane and preparation of both solid and gaseous stable products in various experimental conditions. Therefore, a computer experiment describing the N@sub 2@/CH@sub 4@ plasma was prepared and both the common features and differences of methane decomposition in various types of discharges were discussed. Models consisted of reactions between neutral, charged and excited species. Input data were derived from Langmuir probe measurements and from emission optical spectroscopy. For the solution a macroscopic kinetic approach based on balance equations of individual species was used. In order to reduce the resulting models (consisting of more than 300 and 166 reactions - in active discharges and in flowing afterglow conditions, respectively) a method of reduction of the kinetic scheme was applied. In the discussion the fluxes of carbon and nitrogen atoms were studied in the dependence on concrete experimental conditions and an attention was devoted both to the methodology of simulation and to the reduction technique in plasma chemistry.

#### **PS-TuP8** Diagnostics and Modelling of Ar/O@sub 2@ Plasma used for Plasma Oxidation of Al, J. Pavlik, S. Novak, Z. Stryhal, J. E. Purkyne University, Czech Republic; R. Hrach, V. Hrachova, M. Vicher, Charles University, Czech Republic

Plasma oxidation, utilising highly activated particles in oxygen or oxygen/argon plasma, is one of the low temperature techniques used to growth of dielectric films on metal and semiconductor surfaces. The contribution deals with a comparative study of plasma characteristics and thin oxide film properties with following tasks: to better understand the mechanism of plasma oxidation of aluminium thin films, to find basic factors which play a dominant role in the process studied, and to find factors which determine properties of the created oxide layers. The experiments were carried out in a system for plasma-chemical surface modification of thin films. A DC discharge was applied in an oxygen-argon mixture. The main diagnostic techniques applied in order to determine plasma parameters were the optical emission spectroscopy and the quadrupole mass spectrometry. Both the composition and the atomic surface density of prepared samples were studied by conventional Rutherford elastic back-scattering. Investigation of morphology of the sample surfaces and surface roughness of the alumina thin film were performed by Atomic Force Microscopy. The experimental techniques are combined with computer experiment in order to achieve better insight into the problem solved. The computer experiment consists of several stages model of gaseous plasma chemistry, model of the plasma-solid interaction, and model of processes on the surface of growing oxide film. The technique used was both the macroscopic kinetic approach and combination of various simulation methods - fluid modelling and PIC-MC modelling.

PS-TuP9 Simulation of High Aspect Ratio Trench Profiles in Silicon under a SF@sub 6@/O@sub 2@ Plasma Chemistry by a 2D Surface Model Based on Monte-Carlo Techniques, *G. Marcos*, GREMI, CNRS-Universite d'Orleans, France; *A. Rhallabi*, LPCM, IMN, CNRS-Universite de Nantes, France; *P. Ranson*, GREMI, CNRS-Universite d'Orleans, France

Deep etching to obtain high aspect ratio trenches (deep/width >20) is a current challenge in view of new microelectronic applications. This objective needs a precise control of feature profile evolution during etching, which requires fine comprehension of surface mechanisms occurring. In order to understand consequences on the final etch profile effects due to reactive species in a high density SF6/O2 plasma, we have developed a two dimensional etching model. The species included are fluorine and oxygen radicals and ions which we study the interactions with silicon and mask (SiO2) surface. Angular and energetic distributions of ions are taken into account and calculated using Monte-Carlo simulation of ion transport across rf discharges sheaths. We assume that angular neutral distribution is isotropic. The surface model is based on Monte-Carlo approach allowing move the etched silicon surface by probabilistic criteria. It includes processes such as adsorption/desorption, chemically etching, passivation layer formation, ion preferential sputtering and reflexion, redeposition. The kinetic parameters are introduced as input data using experimentally performed measurements. The silicon area is discretized by a grid and each cell represents really a number of silicon sites. The simulation results show the increase in anisotropy of the etch profile with increasing the ion to neutral flux ratio. Undercut is due to spontaneous etching caused by the isotropic neutral flux. Ion angular distribution and mask geometry appear to be important parameters in the bowing formation. Formation and growth mechanisms of the passivation layer SiOxFy are now known with more accuracy, in function with certain parameters as surface temperature or ion distributions. Its consequences on the final trench topography is also studied.

#### PS-TuP10 Scalability of Innovative ICP Source Geometries, L.J. Pratti, J.M. Marquis, M. Goeckner, L.J. Overzet, University of Texas at Dallas

As industry moves towards plasma processing on larger substrates, there is a need for larger plasma sources. Due to transmission line effects, large traditional planar ICP sources produce non-uniform plasmas, and thus nonuniform processing rates across the substrate. Recently, a threedimensional coil geometry which can reduce these non-uniformities was introduced.@footnote 1@ In this paper, we examine standing wave effects on the field intensities and uniformities when a current node is present on the planar and various 3-D coils. Preliminary experiments show uniformity improves by a factor of 3 or more using the 3-D coil. The location of the node on the coil is found using a dynamic current probe. The field measurements are made with a B-dot probe in the absence of plasma. A separate paper presents the results of a predictive model of the system. @FootnoteText@ This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 009741-0081-1999. @footnote 1@M. H. Khater, L. J. Overzet, Plasma Sources Sci. Technol. 9 (2000) 545-561.

PS-TuP11 Study of Pulsed Plasma Doping by Experimental Diagnostics and HPEM Simulations, Y. Lei, E.A. Oakes, M. Goeckner, University of Texas at Dallas; S.B. Felch, Z. Fang, B.-W. Koo, Varian Semiconductor Equipment Associates

Pulsed plasma doping is a potential solution to implement ultra-shallow junctions. Previous studies of the pulsed plasma doping process have closely examined the implanted species@footnote 1@ and device characteristics.@footnote 2@ In this paper we examine fundamental issues related to the plasma source used in that process. The work reported here combines both experimental and theoretical studies. Experimental work consists primarily of Langmuir probe studies of the discharge. Early data indicate that during a 20  $\mu$ s long implant pulse the plasma density is on the order of 10@super 9@ cm@super -3@ and the electron temperature is ~2 eV. Between pulses, the density falls to 10@super 6@ cm@super -3@ and the electron temperature collapses to ~0.2 eV. We combine the experimental work with simulations using the Hybrid Plasma Equipment Model, HPEM.@footnote 3@ Comparisons will be made between the simulation and the experimental results. Finally, we will discuss likely electron heating mechanisms in this discharge. @FootnoteText@ @footnote 1@M.J. Goeckner, S.B. Felch, Z. Fang, et al. "Plasma doping for shallow junctions," J VAC SCI TECHNOL B 17: (5) 2290-2293 SEP-OCT 1999 @footnote 2@ D. Lenoble, M.J. Goeckner, S.B. Felch, Z. Fang, J. Galvier and A. Grouillet, "Evaluation of Plasma Doping for sub-0.18 µm Devices" Proceedings of the 12th International Conference on Ion implantation Technology '98, Kyoto, Jp, June 22-26, 1998. @footnote 3@

R. Kinder and M. J. Kushner, "Wave Propagation and Power Deposition in Magnetically Enhanced Inductively Coupled and Helicon Plasma Sources", J. Vac. Sci. Technol. A 19, 76 (2001). The authors from UTD gratefully acknowledge M.J. Kushner for allowing us to use HPEM in this study. This work is supported by Varian Semiconductor Equipment Associates.

## PS-TuP12 Neutral Gas Pressure and Flow in High Density Plasmas, M.A. Nierode, D.B. Graves, University of California at Berkeley

The charged species in high density plasmas often couple with the transport processes occurring in the neutral gas. The charged species in the plasma exchange mass, momentum and energy with the neutral species, and under some conditions this can have a profound impact on the neutral processes. We present model results of a neutral gas interacting with a high density plasma. Conservation equations for the neutral species are solved, decoupled from a plasma model, so that the plasma influences the neutral species as specified source terms in the appropriate neutral transport equations. We have included plasma heating, dissociation, and momentum exchange, with the assumed model of a diatomic neutral gas. In particular, we present results for the case of a plasma filling a tube through which a neutral gas flows. Plasma heating and molecular dissociation can have a significant effect on the gas mass-averaged velocity and therefore on the pressure drop in the tube. Depending on how the gas is introduced and pumped, the net effects may differ. In geometries in which gas flow can bypass the region of intense plasma, the effects can be very different. Principles for analyzing various cases are presented.

## PS-TuP14 Numerical Optimization of a C@sub 4@F@sub 8@ Chamber Clean Recipe, G.I. Font, Kinema Research, US; B. Devulapalli, Fluent, Inc.,

US; W.L. Morgan, Kinema Research, US

Plasma deposition reactors are regularly subjected to non-value added cleaning schedules to eliminate build up inside the reactor. Cleaning minimizes flaking and particle shedding which can contaminate or destroy the integrated circuits being created on the wafer. If the cleaning step can be made as fast as possible, the down time for the tool can be minimized. Recently much effort has been devoted to the optimization of plasma reactor clean recipes. The criteria for optimization vary from clean time and expense of feed gas to environmental emissions of PFC's. Parameters which are usually considered for optimization include total gas feed rate, pressure, and mixture ratios of feed gasses. Optimizing studies require costly and time consuming experimentation. If the studies could be conducted numerically, the expense would be greatly reduced. The optimum point could also be tailored for specific reactor geometries. In this work, we use computational methods to optimize a C4F8 chamber clean chemistry. Comparison with experimental results shed light on the viability of conducting such optimizations numerically and give a unique perspective on the change in plasma constituents as the process parameters are varied.

#### PS-TuP16 Computer Modeling as a Tool to Design Non-Critical High Rate Deposition Conditions for the "Baffled Target" Reactive Sputtering Process, T. Nyberg, F. Engelmark, J. Westlinder, S. Berg, Uppsala University, Sweden

Normally it is quite puzzling to operate the target in the high rate metallic mode during reactive sputter deposition. To decrease the target poisoning, several authors have suggested to enclose the target into a box having a front aperture allowing sputtered material to be deposited through the aperture onto the substrates in the main chamber. The purpose of this box is to separate the reactive gas in the chamber from the target thereby decreasing the target poisoning. Non of the previous investigators, however, have made a detailed analysis of the full potential of this novel process design. By basically applying "Bergs' model" for the reactive sputtering process to the conditions valid for this process we successfully were able to predict details of the behavior of the process. Most surprisingly we found out that with this "baffled target" it may be possible to carry out a perfect oxide deposition for a gas supply level even below the supply levels defining the hysteresis region. We have never observed such a favorable behavior for any type of reactive sputtering process before. This behavior offers extremely non-critical processing control allowing non-poisoned target high rate perfect oxide deposition. All our experimental results nicely correlates with the behavior predicted by the computer simulations.

**PS-TuP17 Influence of High Power Densities on the Composition of Pulsed Magnetron Plasmas, A.P. Ehiasarian**, Sheffield-Hallam University, UK, United Kingdom; K.M. Macak, R. New, W.-D. Münz, Sheffield-Hallam University, UK; U. Helmersson, Linköping University, Sweden

The application of high power pulses with peak voltage of -2 kV and peak power density of 3 kW.cm@super -2@ to magnetron plasma sources is a new development in sputtering technology. This study presents evidence of multiply charged Cr and Ti metal ions in the dense plasma region of the high power pulsed magnetron discharge and a substantially increased metal ion production compared to continuous magnetron sputtering. The average degree of ionisation obtained from growth rate measurements of the Cr metal flux generated in the plasma source was 30 % at a distance of 50 cm. The high power is applied to ordinary magnetron cathodes in pulses with short duration of typically some tens of microseconds in order to avoid a glow-to-arc transition. An Ar pressure of typically 0.4 Pa (3 mTorr) is maintained during the discharge. The time evolution within a pulse of the optical emission from Ar@super 0@, Cr@super 0@, Cr@super 1+@, and Cr@super 2+@ showed that at low power (0.2 kW.cm@super -2@) Cr and Ar excitation develops simultaneously. At higher powers (3 kW.cm@super -2@) a distinct transition from Ar to Cr plasma within the duration of the pulse was observed. Optical emission from the various species in the plasma showed an increase in metal ion-to-neutral ratio with increasing power. These observations indicate that a threshold plasma density exists when a transition from conventional pulsed sputtering to pulsed selfsputtering (similar to cathodic arc spots) occurs. First attempts to model the time-dependence of the OES signals are discussed.

#### PS-TuP20 Self-consistent Particle Modelling of Plasma-solid Interaction: Sheath Formation in Electronegative Plasma, *R. Hrach, V. Hrachova, M. Vicher,* Charles University, Czech Republic

Low-temperature reactive plasmas employing electronegative gases are often used for various material processing. Negative ions in such plasmas affect the transport of charged species from plasma to immersed substrates and in this way the corresponding plasma-chemical technologies. The same situation holds for probe diagnostics of lowtemperature plasmas containing negative ions. The derived results depend on various plasma and electrode parameters - as plasma composition, pressure, and form of substrate/probe, etc. - in rather complicated way. In order to simplify the discussion of experimental results a PIC-MC plasma model was suggested and following questions were studied: \* the influence of plasma composition, especially the influence of negative ions, on the distribution of electric potential near the metal substrate \* the influence of pressure on the energy and angular distributions of charged particles in the vicinity of plasma-solid boundary as well as on the fluxes of charged particles on the substrate of solids immersed into plasma \* the dynamical processes taking part in plasma-solid interaction when applying either negative or positive step voltages on the substrate. The simulation was performed for O@sub 2@/Ar plasma in the positive column of dc glow discharge. The attention was devoted both to the calculation of plasma properties together with their comparison with experimentally derived results and to the technique of computer simulation. Computer experiment enabled to discuss various mechanisms in the plasma affecting the distribution of electric potential as well as the fluxes of charged species separately

PS-TuP21 A New Protective Layer Using Plasma Polymerized Thin Films in Plasma Display Panel, S.O. Kim, University of Illinois at Urbana-Champaign, South Korea; G.H. Miley, University of Illinois at Urbana-Champaign

Flat panel displays have recently received much attention in research and development as alternatives to cathode ray tube(CRT). The plasma display panel(PDP) is considered a promising candidate as a conventional display. The performance of ac-plasma display panel(PDP) is influenced strongly by the surface plasma characteristics on the protective layer. The new protective layer in ac-plasma display panel(PDP) manufactured by plasma polymerization is a monomer produced by MMA(Methyl methacrylate). The functional groups of MMA appeard in the PPMMA(Plasma polymerized methyl methacrylate) as well, and this was confirmed through an analysis using FT-IR. The polymerization rate of plasma polymer increased as a function of the plasma power and decreased as a function of the system pressure using scanning electron microscopy(SEM). Plasma polymer has highly secondary electron emission coefficient from 0.02 to 0.14 as a function of the pure Ne ions under accelerating voltage ranged from 50 V to 150 V.

PS-TuP22 Synthesis of Organic Polymer Thin Films by Plasma Assisted CVD for Low k Dielectrics Application, M.-C. Kim, S.-H. Cho, J.G. Han, S.-B. Lee, J.-H. Boo, Sungkyunkwan University, Korea

Plasma polymerized thin films have been deposited on Si(100) substrates at growth temperature between room temperature and 400 °C using thiophene (C@sub 4@H@sub 4@S) precursor by plasma assisted chemical vapor deposition (PACVD) method for low-dielectric device application. In order to compare physical properties of the as-grown thin films, the effects of the plasma power, gas flow ratio and deposition temperature on the dielectric constant and thermal stability were mainly studied. XRD and TED studies revealed that the as-grown thin films have highly oriented amorphous polymer structure. XPS data showed that the polymerized thin films that grown under different RF power and deposition temperature as well as different gas ratio of Ar:H@sub 2@ have different stoichiometric ratio of C and S compared with that of monomer, indicating a formation of mixture polymers. Moreover, we also realized that oxygen free and thermally stable polymer thin films could be grown at even 400 °C. The results of SEM, AFM and TEM showed that the polymer films with smooth surface and sharp interface could be grown under various deposition conditions. From the electrical property measurements such as I-V and C-V characteristics, the minimum dielectric constant and the best leakage current were obtained to be about 3.22 and 10 @super -11@ A/cm @super 2@, respectively.

## PS-TuP23 Improved Gas-mixtures for High Efficiency in AC Plasma Display Panel, *M.-P. Park*, *T.-W Kim*, *H.-J. Hwang*, Chung-Ang University, Korea

In this work, we have examined the Ne-He-Xe gas discharge characteristics in the Plasma Display Panel (PDP) and explained the luminous efficiency at the various gas mixtures. The gas mixtures adopted to the PDP is necessary for both decreasing the power consumption and increasing the luminance efficiency. Therefore, for improving the luminous efficiency significantly in ac PDP, we suggest a new gas-mixtures; (Ne:He=7:3)-(~10%Xe) to achieve good performance for driving waveform as the function of gas pressure, Xe mixing ratio, Ne to He mixture, etc. In addition, the results of experimental measurements have been compared with those calculated by twodimensional FDTD (Finite Difference Time-Domain method) model of the discharge, which is newly applied to our computer code. Through these results, we have found that He mixing ratio and gas pressure led to the decreasing of the delay time and increasing of the luminance efficiency, as Xe gas ratio increases.

#### PS-TuP24 The Effect of Washing Treatments on the Surface Chemistry of Plasma Coated Textiles as Studied by High Resolution XPS, S.R. Coulson, Dera, UK; S.J. Hutton, C. Moffitt, Kratos Analytical, UK

Hydrophobic and oleophobic repellency are highly desirable properties for textiles. Such behaviour can be imparted by coating the surface with perfluoroalkyl polymers. One method of applying such coatings is by plasma polymerisation.@footnote 1@ The advantages of such a solventless method are many and include reduction in waste, low process temperatures and a wide range of suitable substrate materials. However, one problem associated with fluorinated coatings applied to textlies is the loss of liquid repellency during washing. This is attributed to the rearrangement of the fluorinated surface molecules. Here we describe the surface chemistry, as studied by high resolution XPS, of a pulsed plasma deposited fluorinated acrylate before and after washing cycles. @FootnoteText@ @footnote 1@ H. Yasuda, Plasma Polymerisation, Academic Press, London, 1985.

# **PS-TuP25 Surface Reactions of Polyethylene with Nitrogen Plasmas/Ion Beams,** *A.J. Wagner, S.R. Carlo, C. Vecitis,* Johns Hopkins University; *F. Reniers,* Universite Libre de Bruxelles, Belgium; *H. Fairbrother,* Johns Hopkins University

Nitrogen containing functionalities are often introduced into polymer surfaces to improve interfacial properties such as adhesion and biocompatibility. The process of nitrogenation at the molecular level has been probed by investigating the reactivity of polyethylene (PE) with N@sub2@@super+@ ions and N@sub2@ plasmas using X-ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflectance (ATR), Atomic Force Microscopy (AFM) and contact angle measurements. XPS and ATR results indicate that a variety of different nitrogen groups are introduced during the interaction of nitrogen ion beams with PE, notably C-N, C=N, and CN moieties. These chemical modifications are also accompanied by changes in the surface roughness and frictional properties of the interface, as characterized by AFM. These results will be compared with related experiments carried out to determine the change in surface composition of PE as a result of nitrogen plasma and radical treatments.

Titanium atoms have been deposited onto nitrogen modified PE interfaces by physical vapor deposition as a model for an industrial metallization process. The subsequent reactivity of the nitrogenated interfaces with titanium atoms will be discussed in terms of the formation of nitride and carbide species within the interfacial region. To further isolate the reactivity of specific functional groups in bulk polymeric substrates, results will also be presented on the reactivity of a CN terminated self-assembled monolayer with vapor phase titanium atoms.

#### PS-TuP26 Plasma, Electrochemical and Thermal Oxidations of Metals and Alloys as Methods for Designing Nanostructured Oxide Films, J.R. Parga, Instituto Tec. de Saltillo, Mexico; M.A. Hossain, Lamar University; H. McWhinney, Prairie View A&M University; D. Mencer, Penn State University; D.L. Cocke, Lamar University

Plasma, electrochemical and thermal oxidations of metals and alloys are methods of producing functional thin films. However, the fundamental physical chemistry of the film oxidation growth processes have not been sufficiently known to allow design of multicomponent oxide layers. Our reseach has recently determined the factors that control the development of oxide films on metals and alloys by thermal and electrochemical methods from which a predictive model has been developed. We have recently found that plasma methods are quite unique in producing oxide film structures that are not expected from these models. The uniqueness of the plasma method provides an alternative preparation that complements the thermal and electrochemical approaches. Our recent results using various metals and alloys such as Cu, Ni, Al, Zr, Ti and their binary and ternary alloys will be used to delineate the advantages and disadvantages of the three preparation methods and highlight the unique attributes of the plasma oxidation method. Various surface and subsurface characterization techniques have been used to structurally and chemically characterize the resulting films allowing insight into the reasons for the unique behavior of the plasma oxidation. The theoretical background and reaction models which allow structural design at the nanoscale for thermal and electrochemical oxidation will be used to examine the plasma oxidation processes and explore the the predictibility required for oxide film design at the nanoscale.

## **PS-TuP27** Change of Surfaces of PDP Panel during Discharge, K.H. Lee, H. Soh, Y.C. Kim, Hanyang University, Korea

Plasma display panel (PDP) is a most promising candidate for large-area wall-hanging displays because of the features of a simple panel structure and simple processes appropriate for large-area displays.@footnote 1@ Aging process accomplished for 48 hours in PDP fabrication stabilizes the inside of panel and maintains optical performance by initial discharge. We must reduce long aging time for productivity improvement. For these reasons, we investigated an effect which aging process exerts in surface of front panel and rear panel. In this experiment, we developed in-situ analysis system analyzing panel surface without the exposure to minimize the outside influence. This in- situ analysis system can analyze 7 inch test panel. The performance and lifetime of a PDP is strongly related to the MgO protection film, the phosphor layer and discharge gas.@footnote 2@ Therefore, we observed MgO protection film of front panel and Phosphor layer of rear panel according to aging time. Also, in order to find out surface changes according to plasma discharge, 30 minutes aging sample was discharged by He plasma with increasing power. The physical and chemical properties were characterized X-ray photoelectron spectroscopy (XPS), Auger electron microscopy (AES), Atomic force microscope (AFM), Mass spectroscopy (QMS200). @FootnoteText@ @footnote 1@Tsutae Shinoda, Masayuki Wakitani, Toshiyuko Nanto, Noriyuki Awaji and Shinji Kanagu IEEE TRANSATIONS ON ELECTRON DEVICE, vol.47, NO.1, 77 January 2000 @footnote 2@Kunio YOSHIDA, Heiju UCHIKE, Masahiro SAWA, IEICE TRANS.ELECTRON, VOL.E82-C, N10, 1798 (1999)

#### PS-TuP28 Characteristics of Capillary Electrode Atmospheric Pressure Glow Discharge and Its Application to Glass Substrate Cleaning, Y.H. Lee, C.H. Yi, M.J. Chung, G.Y. Yeom, Sungkyunkwan University, Korea

In this study, the characteristics of atmospheric low temperature plasmas generated by capillary electrodes were investigated for the application of the TFT-LCD glass substrate cleaning process. The characteristics of the plasmas were studied as a function of capillary aspect ratios, input power, electrode distance, the gas mixtures of He, O@sub 2@, Ar, and N@sub 2@, etc. using a high voltage probe, a current probe, Quadrupole Mass Spectroscopy (QMS), and optical emission spectroscopy (OES). The voltage between the electrode sincreased 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 the voltage has led to

unstable filamentary discharge from the stable capillary discharge. The use of capillary electrode instead of dielectric barrier electrode (the electrode covered with a non-capillary dielectric) not only decreased the electrode voltage, therefore, increased the stability of the plasma but also increased the discharge current and, therefore, the intensity of the plasma. Increased ionization and dissociation of the plasma species could be observed by OES with the increase of input power in He/O@sub 2@ mixtures. 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@ gas mixtures. Also, using He/O@sub 2@ gas mixtures, organic materials such as photoresist on the glass substrate could be successfully removed with the average etch rates higher than 570 nm/min.

#### **PS-TuP29** The Relationship between Plasma States and Film Formation Behavior in Ti-Me-N by Double Magnetron Sputtering, *Y.M. Kim, J. Kim,* Sungkyunkwan University, Korea, South Korea; *J.G. Han,* Sungkyunkwan University, Korea

The main problems related to a DC reactive sputtering are instability process and low deposition rate. In recent years, in order to overcome these disadvantages, pulsed reactive unbalanced or dual magnetron sputtering is widely used for thin film deposition, such as insulating nitrides and oxides films. In general, for analysis of the influence of plasma parameters on physical properties of thin films, plasma diagnostics have been widely used. In previous works, Ti-N was deposited by unbalanced magnetron sputtering. We have measured plasma parameters during deposition of Ti-N by Langmuir probe and Optical Emission Spectroscopy (OES). As increasing discharge power, plasma density and electron temperature were increased the other side, plasma potential was decreased. In this study, we have developed the mid-frequency powered double magnetron sputtering system with two different material targets. We synthesized Ti-Me-N films with various doped metal contents in this system and analyzed microstructures of the sample with XRD and SEM. Also, for feedback control and analysis of the influence of plasma parameters, we have studied the relationship between plasma states and film formation behavior for double magnetron discharge conditions by Langmuir probe and OES.

**PS-TuP30 Amorphous Metal-organic Chemical Vapor Deposition Nb@sub x@Ta@sub (1-x)@N Films for Diffusion Barrier**, *W.C. Gau, C.W. Wu*, National Tsing Hua University, Taiwan, R.O.C.; *T.C. Chang*, National Sun Yat-Sen University, Taiwan, R.O.C.; *C.H. Li*, National Chiao Tung University, Taiwan, R.O.C.; *C.J. Chu, C.H. Chen*, Nanmat Technology Co., LTD., Taiwan, R.O.C.; *L.J. Chen*, National Tsing Hua University, Taiwan, R.O.C.

To incorporate Cu into interconnection structures, it is necessary to introduce diffusion barrier to prevent Cu from entering the silicon substrate and to form deep level traps. The presence of grain boundaries in the film is generally detrimental to the diffusion barrier properties. One way to eliminate grain boundaries is to render the barrier structure amorphous. In the present work, the resistivity, composition, crystal structure, and microstructure of Nb@sub x@Ta(@sub (1-x)@N film were investigated. Amorphous diffusion barrier of Nb@sub x@Ta@sub (1-x)@N films were deposited in a CVD system with mixed precursors (75% NB= (Net@sub 2@)@sub 4@ and 25% (Net@sub 2@)@sub 3@Ta=NEt ) and NH@sub 3@ gas. The Nb@sub x@Ta@sub (1-x)@N films were deposited at substrate temperatures of 375-500 °C, reactor working pressures of 0.3-0.5 Torr, Argon carrier flow rate of 10 sccm, ammonia reactant flow rates between 5 and 30 sccm. The thermal stability was evaluated by electrical measurement. In addition, the barrier films were deposited onto patterned wafer with 0.2  $\mu m$ -contact holes to check the step coverage. The effects of N@sub 2@/H@sub 2@/NH@sub 3@ gaseous plasma (200W) posttreatment with various times (3-10 min) were also investigated. The films were subsequently characterized by transmission electron microscopy (TEM). Depth profile and the chemical environment of elements in the films were analyzed by x-ray photoelectron spectroscopy (XPS). The amorphous Nb@sub x@Ta@sub (1-x)@N films were found to contain a low C concentration (10%), high N concentration (40%), and low resistivity with NH@sub 3@ as a reactant gas. The resistivity of barrier was increased with time owing to the absorption of oxygen in the atmosphere. NH@sub 3@ plasma post-treatment for 3 min was found to be effective in preventing the oxidation and reducing the resistivity. The Nb@sub x@Ta@sub (1x)@N films were found to be an effective barrier up to 550 °C for 30 min.

PS-TuP31 Silicon Trench Oxidation Layer Formation by Employing Oxygen Negative Ion, H. Shindo, Tokai University, Japan

A low temperature and low damage silicon oxidation technique has been highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. The objective of this work is to study silicon trench oxidation by negative oxygen ion to form an insulation layer for cell isolation. The plasma was produced in a 6 inch stainless-steel chamber, and the downstream plasma was mainly considered because in this region the negative ion was highly populated. Silicon oxidation was made in downstream region, and the stage was biased by the DC voltage as well as the RF bias to irradiate both negative and positive ions. The RF bias voltage was applied to the stage with a cored-transformer, and the secondary of the transformer was biased by DC voltage at the same time. The oxidation experiment was performed at the substrate temperature of 100 to 200 degree C. The frequency of the bias was varied with keeping the RF voltage of 65 V peak-to-peak. The oxidation depth strongly depended on the frequency and there was a limitation of oxidation at both sides of frequency. Since the limitation begins at about 1 MHz which is close to the negative ion plasma frequency, it was concluded that the oxidation was negative ion-assisted. For an application to insulation layer, the breakdown strength of the oxide film thus produced was also examined, and the value of 6.2 MV/cm was obtained. This value is comparable to that of thermally grown oxide film. The trench oxidation showed a farily high directionality which was dependent on the substrate bias voltage. The value of 1.5 were obtained as the oxidation directionality, defined by the ratio of the oxidation depth of the trench bottom to side wall, while with no bias, the directionarilty was only less than 0.5.

#### PS-TuP32 Surface Coating of Poly(meta-phenylene isophthalamide) Nanofibers by Chemical Vapor Deposition and Metal Sputtering, *M. Graham*, *W. Liu*, *D. Reneker*, *E.A. Evans*, University of Akron

Electrospun nanofibers can be used as either functional or sacrificial substrates for creating nanoscale structures. Surface structures of electrospun nanofibers are of great significance for applications in the areas of filtration, biomedicine, catalyst support and electronics. Coating by chemical vapor deposition (CVD) or physical vapor deposition (PVD) offers a straightforward method to modify the surface properties of nanofibers. Using CVD and/or PVD processes surface roughness, chemical composition, mechanical strength, and electrical conductivity can be controlled. Fibers of poly(meta-phenylene isophthalamide) (MPD-I) were commercialized by the Dupont company under the trademark of Nomex®. MPD-I nanofibers were electrospun and collected onto aluminum foil and copper grids as a thin sheet of nonwoven fabric. The average diameter of the as-spun MPD-I fibers was around 200 nm. There was a distribution of fiber sizes. The smallest fiber observed was 4 nm. The fiber surface was relatively smooth. Ultra-thin web-like fibers 3, spring-like fibers and branching fibers were observed, demonstrating the versatility of morphological features produced by electrospinning. Fibers were coated with carbon, copper, aluminum and aluminum nitride using plasma enhanced CVD and PVD processes. TEM, SEM, AFM, and reflectivity measurements were used to characterize the uncoated and coated fibers. MPD-I nanofibers were successfully coated with thin film materials using CVD and PVD processes. The surface features of the fibers were modified so that the roughness, chemical stability, wettability, conductivity and other physical properties of the fiber surface changed or may change accordingly.

#### Plasma Science Room 103 - Session PS1-WeM

#### **Dielectric Etch II**

Moderator: E.S. Aydil, University of California, Santa Barbara

#### 8:20am **PS1-WeM1 Plasma Etching of High Dielectric Constant Materials**, *L. Sha*, *J.P. Chang*, University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as transition metal oxides, to enable their integration in sub-0.13µm complementary metal oxide semiconductor (CMOS) devices. In the work, we aim to study the reaction kinetics of etching zirconium oxide thin films in a high-density chlorine discharge. An Electron Cyclotron Resonance (ECR) microwave reactor is used to generate a chlorine discharge for etching ZrO@sub 2@. The plasma properties, such as the electron density, temperature and distribution, are determined by a Langmuir probe. A gridded ion energy analyzer is built to monitor the ion flux, impinging energy, and distribution. Optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS) are employed to identify the gas phase reactive species, including the reactants (Cl@sub 2@, Cl, Cl@super +@, Cl@super -@, ...) and the reaction products (ZrCl@sub x@, ZrO@sub x@, ...), and quantify their concentrations as a function of the chlorine pressure, substrate temperature, substrate bias, and the plasma source power. Surface reaction chemistry and the etching rate are determined by in-situ transmission infrared spectroscopy and laser interferometry. The reactant neutral to ion flux ratio, a strong function of the processing pressure and the input microwave power, is a key factor affecting the surface reaction chemistry and the etching anisotropy. The concentrations of various ZrCl@sub x@ with different x values are measured and showed a strong dependency on both the reactant neutral to ion flux ratio and the ion incident energy. The surface roughness of the silicon substrate after etching is measured by AFM and compared to that of a pristine silicon surface. The results indicate that the roughness is preserved with lower ion energy, and suggest that the substrate bias should be minimized near the end point.

#### 8:40am **PS1-WeM2 Low-k Etch Selectivity Enhancement Through Ion Energy Control**, *R. Silapunt*, *A.E. Wendt*, University of Wisconsin-Madison; *K.H.R. Kirmse*, *F.G. Celii*, Texas Instruments, Inc.

Organosilicate glass (OSG) is a low-k dielectric material under development for high speed interconnects in integrated circuit manufacturing, but selective etching of OSG over etch stop layers, Silicon Carbide (SiC) and Silicon Nitride (SiN), has proven challenging. Because the energy of ions bombarding the substrate has been shown to play an important role in etch selectivity, it has been proposed that improved ion energy control may provide a solution for improving OSG etch selectivity. However, the conventional sinusoidal substrate bias voltage waveform leads to a broad ion energy distribution (IED), allowing only crude control over average ion energy. Using a narrow IED may significantly enhance selectivity, especially when the ions have energy above the etching threshold energy of one material, but below the threshold energy of the other. We have applied a technique for producing a narrow IED to evaluate its potential for improving OSG/SiN and OSG/SiC etch selectivity. This method replaces the sinusoidal substrate bias voltage waveform with a specially tailored bias voltage waveform consisting of a short voltage spike in combination with longer periods of constant voltage. This produces a nearly constant voltage drop across the substrate sheath and thus a narrow IED. Etching experiments have been conducted in a helicon plasma etching reactor with a C@sub 4@F@sub 8@/Ar/N@sub 2@ gas mixture. A comparison of OSG/SiC and OSG/SiN selectivities between sinusoidal and tailored substrate bias voltage waveform has been made. Etch rates as a function of average ion energy for sinusoidal and tailored bias voltage waveforms show significant differences. With the tailored bias voltage waveform, infinite selectivity is achieved for a 40 V range of bias voltage, while a maximum selectivity of ~2:1 is achieved for the sinusoidal waveform.

#### 9:00am PS1-WeM3 Organic Low-k Film Etching in Inductively Coupled Plasma Employing N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 3@ Gases, H. Nagai, Nagoya University, Japan; M. Hiramatsu, Meijo University, Japan; M. Hori, T. Goto, Nagoya University, Japan

An organic low-k film, FLARE, is one of the most prospective candidates for interlayer films with lower dielectric constants (low-k). N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 3@ plasmas have been used for etching organic low-k film without degrading the film quality and etch profile. In

this study, the organic low-k film was etched in inductively coupled highdensity plasmas (ICP) employing N@sub 2@/H@sub 2@ and N@sub 2@/NH@sub 2@ gases. By changing the mixing ratio of these gases, the anistropic etching profile was obtained. The etching plasmas were evaluated by quadruple mass spectroscopy (QMS), optical emission spectroscopy (OES) technique and microwave interferometer. Furthermore, absolute densities of H and N radicals were measured using the vacuum ultraviolet absorption spectroscopy (VUVAS) employing microplasma as light source. N and H radical densities were estimated on the order of 10@super 11@ - 10@super 12@ cm@super -3@ and 10@super 12@ - 10@super 13@ cm@super -3@, respectively. It was found that the behaviors of H and N radical densities were dependent on H and N atom ratio of feed gases, and were not related to the kind of gases in N@sub 2@/H@sub 2@, N@sub 2@/NH@sub 3@. The behavior of etch rate corresponded to that of H radical density. The correlation between the behavior of radical, ion and electron densities and the etching characteristics of organic low-k film is investigated. On the basis of these results, the mechanism for anisotropic etching and the surface reaction of radicals on organic low-k film are discussed.

#### 9:20am PS1-WeM4 Study of Surface Reaction on Organic Low-k Dielectric Etching By Plasma Beam Irradiation, Y. Yamaoka, K. Kurihara, K. Karahashi, M. Sekine, M. Nakamura, ASET, Japan

Etching of low-k dielectrics is one of the most critical processes for the next ULSI fabrication. Etching mechanism of a poly arylene ether (PAE), which is one of the organic low-k dielectrics, was investigated by using a plasma beam irradiation apparatus. The apparatus can control ion flux density (@GAMMA@i), neutral flux density (@GAMMA@n) and ion energy (Ei), independently. The controlled plasma beam was irradiated to the PAE coated on Si substrate in an irradiation chamber, and etch rates (ERs) and desorbed products were measured. The beam was extracted from an ECR type plasma chamber with a N@sub 2@ gas. The @GAMMA@i was controlled by changing the ion beam diameter using an electrostatic focusing lens. The @GAMMA@n was changed by altering the distance between the plasma chamber and the substrate. The Ei was adjusted by DC bias applied to the plasma chamber. Pressures in the plasma and the irradiation chamber were 4 mTorr and 1 x 10@super -6@ Torr during the beam irradiation, respectively. The dominant species in the incident beam were N@sub 2@ and N@sub 2@@super +@. The ER measurements were performed at an incident angle of 0° to the substrate surface normal (@theta@ = 0°). The ERs increased with increasing @GAMMA@n at the constant @GAMMA@i and Ei. The increase of ERs could be attributed to that of the @GAMMA@n. When @GAMMA@i and @GAMMA@n were kept constant, higher ERs were obtained at higher Ei in the range from 500 to 700 eV. Desorbed species of m/e < 100 during the beam irradiation with @theta@ = 50° were measured by a quadruple mass spectrometer. Signals of m/e = 26 (CN), 27 (HCN) and 52 (C@sub 2@N@sub 2@) were observed as etched products directly desorbed from the substrate surface. Effects of H@sub 2@ gas addition on the desorbed products formation and the ERs will be discussed. @FootnoteText@ This work was supported by NEDO.

#### 9:40am **PS1-WeM5 Low K Porous Silica Etch Behavior in Inductively Coupled Discharges,** *M. Barela***, University of New Mexico, U.S.;** *H.M. Anderson***, University of New Mexico**

Low k dielectric films are of interest to the semiconductor industry as a part of the overall solution to minimize RC time delays in the ever-shrinking critical dimensions in modern semiconductor products. We have examined the etching characteristics of several representative porous silica surfaces in an industrially relevant high-density, low-pressure fluorocarbon plasma environment. These characteristics include etch rate, selectivity to Si and photoresist, etch isotropy, and etch stop. We determined that the bias power strongly influences etch rate and selectivity. It was found that the surface-plasma interaction has a strong effect on the growth of the thin fluorocarbon film which is known to mechanistically to control the etch process under optimal conditions of high etch rate and good selectivity to other materials. Furthermore, the porous nature, and modified chemical structure of the silica film has unique interactions with the etching plasma. We determined that porous silica films, where hydroxyl groups terminate surface sites, require higher bias in order to etch in comparison to similar porous silica films, which have been fluorinated. The hydroxylated surface scavenges fluorine creating a carbon rich polymer film which leads to premature etch stop and increased aspect ratio dependence etching (ARDE). FTIR and IRLAS were used to illuminate key differences in the modified surface and gas phase species in the plasma, as compared to conventional dense silica.

10:20am **PS1-WeM7 Etching Mechanism in High-aspect-ratio Contact Hole Etching**, *N. Negishi, M. Izawa, K. Yokogawa, Y. Momonoi, H. Kawahara, S. Tachi*, Hitachi Ltd., Japan; *J. Ghormley*, Hitachi America Ltd.

As it advances beyond the 0.1-µm design rule, ULSI fabrication will require highly selective contact hole etching with high aspect ratio of over 15 and a bowing-free etched shape. To meet these requirements, the etching mechanism in high-aspect-ratio contact hole was investigated in terms of the transport of radical in a hole by using ultra-high-frequency ECR (UHF-ECR) plasma etching system@footnote 1@ with an Ar/C @sub 5@F@sub 8@/O@sub 2@ gas mixture. In this investigation, we assumed the dissociation species in this plasma are CF@sub 2@, C, F, and O. Under this assumption, almost no protective film is formed on the middle part of the hole sidewall and bowing occurs around this point. To accumulate a protective sidewall film, we increased the amount of CF@sub x@ radicals whose sticking-coefficient is low and reduced the sticking-coefficient of C radicals, so the bowing was reduced by 73%. Moreover, the distribution of C intensity was found to have a peak at a sidewall aspect ratio of around 4 in an etched hole by auger electron spectroscopy. This result can be explained by taking account of the transport of high-sticking-coefficient radicals such as C, deposition removal by O and F radicals, and radical reflection at the sidewall in a hole. Thus, we consider that the unexpected etch-stop occurs at an aspect ratio of around 4 when oxygen flow rate or ion energy is a little low. However we found that a contact hole can be formed without etch-stop and mask selectivity can be improved by step etching, during which oxygen flow rate was reduced at an aspect ratio of over 4. Accordingly, a 0.09-µm-diameter contact hole with an aspect ratio of 22 and a resist mask selectivity of over 13 was formed directionally. @FootnoteText@ @footnote 1@ K. Yokogawa, N. Negishi, S. Yamamoto, K. Suzuki, and S. Tachi, 1997 Dry Process Symp., pp 379-383.

#### 10:40am **PS1-WeM8 Optimization of a Nitride Etch Process Using Optical Detection of NO**, F.G. Celii, C. Huffman, Texas Instruments, Inc.; J. Hosch, Verity Instruments

With many copper backend integration schemes, silicon nitride (SiN) etch stop lavers are etched over copper. Because of misalignment, the SiN etch may also occur over oxide, where high selectivity to oxide would be desired. Typical plasma conditions use fluorocarbons with O@sub 2@ or Ar at low plasma power, which avoids Cu sputtering; however, the selectivity to oxide is typically low (~2:1). Etch conditions in a remote plasma reactor have been reported which give higher nitride:oxide selectivity based on the role of NO to enhance etching of SiN.@footnote 1@ We report the use of optical emission spectroscopy to optimize NO concentration in N@sub 2@/O@sub 2@/Ar plasmas, with or without a fluorocarbon source, for use in SiN etching. Signature spectra of excited molecular (N@sub 2@\*, NO\*) and atomic (O\*, Ar\*) species were identified and tracked over various plasma conditions in a commercial etch reactor. Small corrections were made using the Ar\* intensities. While the relative concentrations of N@sub 2@\* and O\* species are linear with N@sub 2@ and O@sub 2@ flow, the NO concentration shows a maximum which occurs at a flow ratio of ~90/10 N@sub 2@/O@sub 2@. Survey etch experiments were run with blanket oxide and nitride wafers, using conditions of maximum NO concentration. Variation of the other process conditions showed that decreased bias power, along with increased NO and F conditions, lead to increased nitride/oxide selectivity, including values higher than the baseline process. The extension of this work to include profile and etch rate results from patterned nitride and nitride/oxide wafers will also be reported. @FootnoteText@ @footnote 1@ B. E. E. Kastenmeier, P. J. Matsuo and G. S. Oehrlein, J. Vac. Sci. Technol., A17 (1999) 3179.

# 11:00am PS1-WeM9 Ultra High Selective Silicon Nitride Etching with a Downstream Remote Plasma using CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@, S. Halle, K. Wilson, K. Settlemyer, IBM Microelectronics; H. Kimura, Shibaura Technology International Corp.

A silicon nitride etch process with ultra high selectivity to silicon oxide has been developed with CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@/X, where X = Ar, N@sub 2@, or no buffer gas, using remote plasma chemical downstream etching. The application of an ion damage free, isotropic removal of a silicon nitride film over thin oxide has been limited to date due to the lack of a ultra high selective dry strip process with a high etch rate and good cross wafer uniformity. In contrast to previously reported work, the CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@/X process achieves an oxide selectivity > 70:1, while maintaining a high silicon nitride etch rate >200 nm/min and a uniformity  $\sim$  3% 1@sigma@. The addition of CH@sub 2@F@sub 2@ to the well characterized microwave discharge of CF@sub4@/O@sub 2@ and CF@sub 4@/O@sub 2@/CH@sub 2@F@sub 2@F@sub 2@ is found to increase the silicon nitride etch by a factor of 4 and 2, while

maintaining an oxide etch rate of approximately 60-70 and 30-40 Å/min, respectively. Although a small amount of N@sub 2@ addition to a CF@sub 4@/O@sub 2@ plasma has been shown to significantly enhance the silicon nitride etch rate, only in the regime of N@sub 2@/(N@sub 2@+O@sub 2@) > 0.4 does the etch rate linearly increase with N@sub 2@ addition. A film deposition, post etching, on the wafer surface is found to be water soluble. In addition, the silicon nitride etch rate decreases by a factor of 5 as the wafer temperatures increases from 50 to 70C. Experimental observations are consistent with a reactive surface layer mechanism, whereby an enhanced silicon nitride etch rate is achieved as the layer is thinned in the presence of nitric oxide (NO).

#### Plasma Science Room 104 - Session PS2-WeM

#### Modeling

#### 8:20am PS2-WeM1 Time-Dependent Electron Impact Source Functions in Inductive and Capacitive Plasma Sources Obtained Using an "On-The-Fly" Monte-Carlo Technique@footnote 1@, A. Sankaran, M.J. Kushner, University of Illinois

Electron temperatures in low-pressure inductively and capacitively coupled plasma reactors do not significantly vary during the rf cycle. There can be, however, considerable modulation of rate coefficients and source functions for electron impact reactions having high threshold due to modulation in the tail of the electron energy distribution at energies which are less collisional. Since the character of this modulation requires that the electron energy distribution (EED) be resolved, we developed a new "On-the-Fly" (OTF) Monte-Carlo technique to compute the time dependent properties of EEDs. Using this method, Fourier frequency coefficients of the moments of the EEDs are obtained as a function of position in the reactor. The time dependence of the resulting electron impact processes are then reconstructed as a time series. The OTF method was incorporated into the Electron Monte Carlo module of a 2-dimensional plasma equipment model. The time and spatial variation of low and high threshold processes in rare gas/molecular gas mixtures will be discussed, comparing systematic trends in ICP, capacitive and helicon plasma sources. In ICPs, we found that time dependence of high threshold events such as ionization are dominated by even harmonics, whereas in asymmetric CCPs, odd harmonics are also important. The harmonic content of sources increases with increasing threshold energy and pressure. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials

#### 8:40am PS2-WeM2 Global Neutral Modeling of Fluorine Plasma Etching for MEMS Applications, *R.L. Jarecki*, *M.G. Blain*, *R.J. Shul*, Sandia National Laboratories

The advent of time-sequenced processes featuring alternating fluorocarbon (i.e. C@sub 4@F@sub 8@) deposition and fluorine-based (i.e. SF@sub 6@) etching steps for very deep (@>=@100  $\mu$ m) and maskselective (@>=@100:1) etching of silicon@footnote 1@ has made fabrication of advanced bulk MEMS (micro-electro-mechanical systems) devices much more feasible. This intriguing new application suddenly makes the fundamental process of ion-assisted etching of silicon by atomic fluorine of much greater research interest. In this work, a simple continuous stirred tank reactor (CSTR) framework has been used to model representative neutral species in an inductively-coupled etch tool during SF@sub 6@/Ar plasma etching. The well-established technique of actinometry has been employed to assess the mean relative fluorine concentration by ratioing the FI (703.7 nm) and ArI (750.4 nm) atomic line emission collected by an optical multichannel analyzer (OMA). A strong correlation of the pressure rise upon discharge, at fixed throttle valve position, to actinometric fluorine concentration has been observed, in agreement with the CSTR model. Silicon etch rates have also been measured. By testing a range of source powers, throttle valve positions, and flowrates, the fluorine losses for a particular reactor can be characterized to complete the CSTR model. Such a model makes possible reasonable extrapolations of fluorine concentration, and hence silicon etch rate, and can potentially speed evaluation of ultimate process limits for a given hardware configuration, as well as facilitate etch process development.@footnote 2@ @FootnoteText@ @footnote 1@U.S. Patent 5,501,893, Laermer, et al., March 26, 1996. @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.

9:00am PS2-WeM3 Instabilities in Low-Pressure Electronegative Inductive Discharges, P. Chabert, Ecole Polytechnique, France; A.J. Lichtenberg, M.A. Lieberman, A.M. Marakhtanov, H.B. Smith, University of California, Berkeley; M. Tuszewski, Los Alamos National Laboratory

Plasma instabilities are sometimes seen in commercial inductive processing tools with attaching gas feedstocks. We have studied these instabilities experimentally in low-pressure inductive discharges with Ar/SF6 mixtures using optical emission, Langmuir probes, microwave diagnostics, neutral and ion mass spectrometry, a fast video camera, and voltage-current sensors. The onset of instability as a function of pressure and driving power was explored for gas pressures between 2.5 and 100 mTorr and absorbed powers between 150 and 1200 W. The frequency of the oscillations increases with pressure and lies between 1 and 100 kHz. At a given pressure, there is a power window at the transition from capacitive to inductive modes where oscillations are seen in charged particle density. electron temperature and plasma potential (the unstable region). The instability window gets smaller as the argon partial pressure increases. The settings of the matching network influence the frequency of the instability. We have improved a previously developed volume-averaged (global) model to describe the instability. We consider a cylindrical discharge containing time varying densities of electrons, positive ions, negative ions, and time invariant excited states. The driving power is applied to the discharge through a conventional L-type capacitive matching network, and we use realistic models for the inductive and capacitive energy deposition and the particle losses. The particle and energy balance equations are integrated, considering quasi-neutrality in the plasma volume and charge balance at the walls, to produce the dynamical behavior. As pressure or power is varied to cross a threshold, the instability is born at a Hopf bifurcation, with relaxation oscillations between higher and lower density states. The model qualitatively agrees with experimental observations, and phase plane portraits of the dynamics found experimentally and theoretically are in good agreement.

#### 9:20am PS2-WeM4 3-Dimensional Modeling of Asymmetric Gas Heating in Plasma Processing Reactors@footnote 1@, P. Subramonium, M.J. Kushner, University of Illinois

As wafer sizes increase, obtaining uniform processing conditions becomes more problematic particularly with respect to side-to-side asymmetries. Side pumping or gas injection produces asymmetries not only in the gas density but also in ion temperatures and fluxes. As a major source of gas heating is momentum transfer from ions, small asymmetries in ion temperatures are amplified through asymmetries in gas pressure. To investigate the consequences and prevalence of asymmetric gas heating and gas temperatures, a 3-dimensional plasma equipment model was improved by adding multi-fluid modules for gas and ion temperatures. A temperature is computed for each neutral and heavy particle species, while accounting for convective transport, conduction, compressive heating, sources, momentum exchange between species and temperature jumps at surfaces. As ion heating occurs dominantly in the presheath, we found that asymmetries which perturb the presheath produce gradients in ion temperature which in turn produce gas heating. Somewhat counterintuitive, we therefore find higher gas temperatures near ports due to there being higher ion temperatures in the presheath. We will also discuss the consequences of 3-dimensional coil structures on gas heating. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

#### 9:40am PS2-WeM5 Electron-Molecule Collisions in Processing Plasmas@footnote 1@, V. McKoy, California Institute of Technology INVITED

In the plasmas that are widely used in semiconductor fabrication, inelastic collisions between low-energy electrons and polyatomic gases are the principal mechanism for the production of the reactive species responsible for etching and other processes at wafer surfaces. An understanding of the behavior of these plasmas thus depends on knowledge of the relevant electron-molecule collision cross sections. However, such cross sections, particularly those for the production of neutral fragments, are difficult to measure or to calculate and are often unknown for gases of interest. Over the past several years we have been exploiting large-scale parallel computers to calculate electron-collision cross sections for numerous flurocarbon feed gases and their radicals. In this talk, I will give an overview of these calculations and examples of the results we have obtained. @FootnoteText@ @footnote 1@Work supported by Sematech, Inc. and Intel Corp. and done in collaboration with Carl Winstead and M. H. F. Bettega.

#### 10:20am PS2-WeM7 Ionization Mechanism in ICPs, F.F. Chen, UCLA

Inductively coupled plasmas with antennas wrapped around the radial surface of a cylinder are known to produce uniform plasma density profiles even though the skin depth is smaller than the discharge radius. The penetration of rf energy into interior regions has been attributed to the anomalous skin effect, in which thermal motions carry ionizing electrons past the skin layer,@footnote 1@ or to the nonlinear generation of 2nd harmonic currents.@footnote 2@ We have computed the orbits of electrons starting at arbitrary positions as they are accelerated and decelerated at different rf phases. Elastic and inelastic collisions are taken into account, and electrons are reflected when they strike the wall sheath unless they have sufficient energy to penetrate it, in which case they are lost and replaced by a slow electron elsewhere. The nonlinear Lorentz force preferentially pushes fast current-carrying electrons toward the axis. This effect, coupled with reflections from the curved wall, generates a population of fast, ionizing electrons distributed throughout the discharge. This dominant mechanism eliminates the need to place antenna elements at small radii. @FootnoteText@ @footnote 1@V.A. Godyak and V.I. Kolobov, Phys. Rev. Lett. 81, 369 (1998). @footnote 2@R.B. Piejak and V.A. Godyak, Appl. Phys. Lett. 76, 2188 (2000).

#### 10:40am PS2-WeM8 A 3-dimensional Model for Wave Propagation and Plasma Properties in Magnetically Enhanced ICP Reactors@footnote 1@, *R.L. Kinder*, *M.J. Kushner*, University of Illinois

Electromagnetic wave propagation in magnetically enhanced inductively coupled plasmas (MEICPs) enables power deposition to occur remotely from the coils and at locations beyond the classical skin depth. 3dimensional, azimuthally symmetric components of the electric field can be produced by an azimuthally symmetric (m=0) antenna in flaring solenoidal static magnetic fields. Asymmetric antennas (m=+1,-1) produce 3-d components of the electric field lacking any significant symmetries, and so must be fully resolved in 3-dimensions. To investigate these processes, a 3dimensional plasma equipment model was improved to resolve 3-d components of the electric field produced by m=+1,-1 antennas in flaring magnetic fields. A tensor conductivity was used to couple the components while solving the wave equation in the frequency domain using an iterative, sparse matrix technique. For gas pressures of 2-20 mTorr, magnetic fields of 10-300 G, we observe rotation of the electric field downstream of the antenna where significant power deposition also occurs. Feedback from the plasma which produces local extrema in conductivity (e.g., ionization rates and electron temperatures peak where fields are largest) result in the electric field patterns not having pure modal content. Comparisons for electron density and temperature will be made to probe measurements made in a MEICP having a helicon source. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials

#### 11:00am PS2-WeM9 Modeling of Fundamental Processes in a Capacitively Coupled Helium Atmospheric-Pressure Glow Discharges, X. Yuan, L.L. Raja, Colorado School of Mines

Stable, large-volume, non-equilibrium plasmas, called Atmospheric-Pressure Glow Discharges (APGD), are emerging as an important new class of glow discharges with several potential applications in materials processing. These discharges operate in a previously inaccessible regime of the plasma parameter space, where properties resemble low-pressure glow plasmas but at significantly higher (atmospheric) pressures. Recently, several investigators have reported the generation of large-volume APGD and uses of APGD in the processing of materials. However, there exists no clear explanation of the structure of these discharges and the reasons for their stability. This paper reports detailed one-dimensional model-based investigation of a capacitively coupled APGD. The paper will discuss the structure of these highly collisional, non-equilibrium plasmas and the chemical nature of these discharges. Model predictions of the stability boundaries of the discharge will be reported. Results show that for certain operating conditions and working gas compositions, stable operating regimes between breakdown and arcing are obtained. Model predictions for discharge V-I characteristics and the stability boundaries are compared to experimental results reported in the literature. @FootnoteText@ This work is supported by a NSF-CAREER Award.

#### 11:20am PS2-WeM10 A Novel Approach for Control of High-Density Plasma Process Parameters through Optimal Pulse Shaping, *T.L. Vincent*, *L.L. Raja*, Colorado School of Mines

Increasingly stringent requirements in the manufacture of Integrated Circuits (IC) are demanding new approaches for the design and operation of semiconductor process equipment and plasma process equipment in

particular. Indeed, several novel plasma process techniques have been proposed recently, one of which is the operation of plasma reactors in a pulsed mode. In this approach, the main ICP power to a High-Density Plasma (HDP) reactor is deliberately modulated using square-wave pulses to provide control of plasma process characteristics. Square-wave pulsed operation has been demonstrated to improve etch/deposition rates of thin films, etch selectivity, and process uniformity. In this study, we propose a completely general technique, called "pulse shaping", for the dynamic operation of plasma reactors. Pulse shaping uses a numerical optimal control methodology for the systematic design of power modulation waveforms to achieve user-specified plasma process conditions. In the work discussed here, a time-dependent global model for an argon HDP reactor is used in conjunction with an optimal control algorithm to demonstrate that optimal design of pulse shapes can be achieved to simultaneously control time-averaged bulk plasma electron temperature and active species composition. Results are presented to illustrate the potential for significantly improved control of plasma characteristics over simple square-wave modulation of reactor power.

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#### Plasma Science Room 104 - Session PS-WeA

#### **Plasma Surface Interactions II**

Moderator: E.R. Fisher, Colorado State University

#### 2:00pm PS-WeA1 Laser Desorption-Laser Induced Fluorescence In situ Studies of Si Etching in Inductively-Coupled Cl@sub 2@-Ar Plasmas, *N.C.M. Fuller*<sup>1</sup>, Columbia University; *V.M. Donnelly*, Agere Systems; *I.P. Herman*, Columbia University

Laser desorption-laser induced fluorescence (LD-LIF) is used to determine the surface coverage of chlorine during the steady-state etching of Si in an 18 mTorr inductively-coupled Cl@sub 2@-Ar plasma as a function of the rf power, substrate bias and Cl@sub 2@ fraction. Laser repetition rate studies, which indicate how the surface is re-chlorinated between laser pulses after each step of laser desorption of surface SiCl@sub x@, reveal that close to steady-state chlorination is achieved in the 10 ms time between 308-nm laser pulses (at 100 Hz) even with only 6% Cl@sub 2@ (94% Ar). This is not unexpected given our prior work in neat Cl@sub 2@ plasmas, for which there is near steady-state chlorination between such laser pulses at 1 mTorr pressure. A mechanism for the competitive etching processes of chlorination (mostly by Cl atoms in the bright mode) and surface sputtering (mostly by Ar and Cl positive ions) will be presented, by coupling these surface adlayer measurements with the etch rates and the optical emission actinometry determination of the densities of the major neutral and positive ions in the plasma.

# 2:20pm **PS-WeA2 Monitoring Plasma-Wall Interactions During Etching of Thin Film Stacks**, *S.J. Ullal*<sup>2</sup>, University of California, Santa Barbara; *H. Singh, J. Daugherty, V. Vahedi*, Lam Research Corporation; *E.S. Aydil*, University of California, Santa Barbara

Surface reactions on plasma etching reactor walls affect the species concentrations in the discharge and plasma properties such as electron temperature and ion flux. Despite the importance of plasma-wall interactions, reactions occurring on surfaces in contact with the plasma are poorly understood and wall conditions are uncontrolled during etching. Often, a stack of thin films of different materials must be etched sequentially in the same reactor using different gases. Complex multilayered films are deposited on the chamber walls during the etching of the stack and interaction between successive etching steps through the changing wall conditions may have deleterious effects. 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 as a diagnostic to monitor the films and adsorbates on the walls of an inductively coupled plasma etching reactor. Using this probe we studied the shallow trench isolation etching of Si where a photoresist patterned stack of anti-reflection coating, Si@sub 3@N@sub 4@, SiO@sub 2@ and Si is etched sequentially using gases as varied as fluorocarbons, Cl@sub 2@, HBr, and O@sub 2@. During the fluorocarbon etching of Si@sub 3@N@sub 4@ and SiO@sub 2@, fluorocarbon films deposit on the chamber walls. During the subsequent etching of Si by Cl@sub 2@/O@sub 2@, etch products such as SiCl@sub x@ react with the O in the plasma and deposit a silicon oxychloride layer on the reactor walls on top of the fluorocarbon layer. In order to maintain etching reproducibility, these multi-layered films must be cleaned before the next wafer is etched in the chamber. Reactions occurring on the wall surfaces and strategies to remove these complex multi-layered films to maintain reproducibility of wall conditions and etching processes will be discussed.

#### 3:00pm **PS-WeA4 Controlling the Ion Flux and Energy Distributions in LAPPS@footnote 1@**, *S.G. Walton*, *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 fluxes to a conducting electrode surface in NRL's Large Area Plasma Processing System (LAPPS) are presented. In LAPPS, a high-energy electron beam is used to ionize a background gas, producing a plasma over the volume of the beam. The beam is generated by a linear hollow cathode and magnetically collimated which allows for the production of uniform plasmas over areas up to 1 m@super 2@ or more. Electron beams are efficient at producing high-density plasmas (10@super 10@-10@super 12@ cm@super -3@) at

low temperatures (Te < 1.0 eV) and are decoupled from the reactor geometry. Hence, control over the flux and incident ion energy at independently located and biased electrodes is possible and advantageous in dry processing applications. Temporally resolved ion flux and energy distributions at an electrode surface are reported for pulsed discharges in noble and molecular gases. The flux, sampled through a small orifice located in the center of the electrode, is analyzed via an energy selector in series with a mass spectrometer. Measurements are presented for a grounded and RF-biased electrode as a function of operating pressure, source-electrode separation, and the applied bias. In argon for example, the incident Ar@super +@ energy is pressure dependent and found to scale with the applied RF bias. In molecular gases, the magnitude and composition of the flux is dependent upon the source-electrode separation and found to vary in time, particularly in the afterglow. The results are discussed in terms of processing applications. Additional details concerning LAPPS are presented by co-authors at this conference.@footnote 2@ @FootnoteText@ @footnote 1@ Work supported by the Office of Naval Research @footnote 2@ See presentation by D. Leonhardt and D.D. Blackwell. @footnote \*@S.G. Walton: SFA, Inc.; D.D. Blackwell: NRC Postdoctoral Research Associate

3:20pm PS-WeA5 High-Density Plasma-Based Etching of Organosilicate Glass (OSG) in C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ Gas Mixtures: Process Results and Diagnostics, *M. Fukasawa*, X. Li, X. Wang, L. Ling, G.S. Oehrlein, University of Maryland, College Park; F.G. Celii, K.H.R. Kirmse, Texas Instruments, Inc.

We report gas phase and surface studies of high-density plasma etching processes of organosilicate glass (OSG), a low-k oxide, and Si@sub 3@N@sub 4@ and SiC etch stop materials, in C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ gas mixtures. Owing to the presence of methyl groups in the SiO@sub 2@ backbone the etching behavior of OSG differs significantly from that of conventional SiO@sub 2@. The addition of O@sub 2@ can be used to increase the OSG etching rate (e.g. from 900 nm/min for a 1400 W 6 mTorr C@sub 4@F@sub 8@ discharge and a selfbias voltage of -85 V to 1100 nm/min for C@sub 4@F@sub 8@/20% O@sub 2@), but can modify the OSG material by oxidizing methyl groups and reduce the selectivity to the etch stop material. The goal of this work was to establish the key variables that can be used to maximize the etch selectivity of OSG with respect to the etch stop materials while minimizing the OSG modifications. An inductively coupled high-density plasma etching reactor equipped with in situ ellipsometry, optical emission spectroscopy (OES) and mass spectrometry was used. Measurements were made as a function of C@sub 4@F@sub 8@/Ar and C@sub 4@F@sub 8@/O@sub 2@ gas composition for pressures ranging from 6 to 20 mTorr, source power levels up to 1400 W, and as a function of RF bias. Both blanket film etching of OSG, SiO@sub 2@, Si@sub 3@N@sub 4@ and SiC and transfer of hole/trench patterns into OSG were studied as a function of process conditions. We utilized the gas phase characterization results, and X-ray photoelectron spectroscopy (XPS) data of etched films after vacuum transfer, to explain the observed etching behavior, evaluate surface/bulk modifications of the OSG vs. process conditions, and identify the critical factors that enable high quality pattern transfer processes of OSG over Si@sub 3@N@sub 4@ and SiC.

#### 3:40pm PS-WeA6 Plasma Deposition of Silicon Thin Films: Atomic-Scale Modeling of Radical-Surface Interactions, D. Maroudas, University of California, Santa Barbara INVITED

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasmaassisted deposition from silane-containing discharges are used widely in technological applications. A fundamental understanding of the interactions of radicals, such as SiHx (0<x<4) and H, with the growth surface is required for the development of improved a-Si:H deposition strategies. Toward this goal, we have developed a hierarchical atomic-scale modeling approach for identification and analysis of the interactions between silane fragme nts and silicon growth surfaces and for systematic characterization of the computationally generated a-Si:H films. This approach combines classical molecular-dynamics (MD), molecular-statics, and Monte Carlo simulations with quantum mechanical calculation s of surface reaction energetics based on density functional theory. Our MD simulations of radical impingement on the growth surface reveal several classes of surface reactions that occur during amorphous film deposition and their role in the growth proce ss. Surface hydrogen is removed by abstraction reactions according to Eley-Rideal or Langmuir-Hinselwood mechanisms. Silicon is incorporated into the growing film through radical attachment to surface dangling bonds, as well as radical insertion into Si-Si surface bonds including dissociative adsorption reactions. In addition, reactions that

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involve Si-Si bond formation between adsorbed species are identified and analyzed. Various surface migration mechanisms for mobile surface species also are discussed. The simulated evolution of the film's structure, surface morphology and roughness, surface reactivity, and surface composition is analyzed systematically. Finally, our simulation results are compared with experimental measurements based on ATR-FTIR spectroscopy for the temperature dependence of the H coverage of the surface and surface hydride content. The comparisons are used to discuss our current understanding of the deposition mechanism.

4:20pm PS-WeA8 Molecular Dynamics Simulations of Ar@super +@-Si and Si:F Interactions, *D.B. Graves*, *D. Humbird*, University of California at Berkeley

4:40pm PS-WeA9 Atomic-Scale Simulation Study of the Role of H Atoms in the Amorphous to Nanocrystalline Transformation in Plasma-Deposited Silicon Thin Films, S. Sriraman, E.S. Aydil, D. Maroudas, University of California, Santa Barbara

Hydrogenated amorphous (a-Si:H) and nanocrystalline (nc-Si:H) silicon thin films grown by plasma deposition from SiH@sub 4@ and H@sub 2@ containing discharges are widely used in photovoltaic and flat-panel display technologies. When an a-Si:H thin film is exposed to a H@sub 2@ plasma, its nanostructure changes from amorphous to nanocrystalline. Though several hypotheses have been proposed, the fundamental mechanisms behind this transformation are still not well understood. Molecular dynamics (MD) simulations of the interactions of thermal and energetic H atoms with a-Si:H films and their surfaces are used to elucidate the nanoscopic mechanisms behind the amorphous to nanocrystalline transformation. a-Si:H films are deposited through MD simulations of repeated impingement of individual SiH@sub 3@ precursors on an initial H-terminated Si(001)-(2x1) surface. H@sub 2@ plasma exposure is simulated through repeated impingement of individual H atoms onto these a-Si:H films grown by MD. Of the many elementary surface reactions that were identified, Eley-Rideal type H abstraction reactions are believed to mediate strain relaxation processes and promote amorphous to nanocrystalline transformation. The effects of abstraction reactions on the growth surface are examined by analyzing their influence on both local and overall film structure. The surface hydride compositions in the deposited films before and after exposure are compared with experimental data and the comparisons are used to discuss our current understanding of the amorphous to nanocrystalline transformation.

#### 5:00pm PS-WeA10 A Fast Computational Model for Study of Coupled Bulk Plasma-Sheath-Bias Circuit Phenomena and its Effect on Plasma-Surface Interactions, *L.L. Raja*, Colorado School of Mines; *E. Meeks*, Reaction Design, Inc.

High-density plasma reactors are used extensively in the etching and deposition of thin films in the manufacture of large-scale integrated circuits. With feature sizes approaching 0.1 microns and lower, it is increasingly important to develop quantitative understanding of plasmasurface interactions and their dependence on plasma reactor geometry, operating conditions, and bias-circuit settings. Of critical importance is the relationship between reactor controls and ion impact phenomena such as the Ion Energy and Angular Distribution Functions (IEDF and IADF). We have developed a new fast computational software tool that enables prediction of IEDF and IADF in high-density plasma reactors through coupling of bulk plasma, RF sheath, and bias circuit models. We simulate the bulk plasma using the well mixed reactor model, AURORA,@footnote 1@ while the RF sheath sub-model uses a multiple-ion extension of the Riley sheath model@footnote 2,3@ coupled to a typical bias circuit model, based on first-principles. The coupled model handles detailed gas-phase chemical reactions that are characteristic of process plasmas and can predict multiple ion IEDFs and IADFs as a function of reactor geometry, and reactor and bias circuit settings. The general surface-chemistry capability allows for specification of ion-energy dependent yields for ion-enhanced surface reactions. The coupled model executes within minutes on a personal computer, providing a fast simulation tool for quickly exploring alternative process conditions and reactor designs. Example results in a fluorocarbon plasma etching system will be reported. @FootnoteText@ @footnote 1@R. J. Kee, F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, et al., Chemkin Collection 3.6, (Reaction Design, Inc., San Diego, CA, 2000) @footnote 2@M. E. Riley, Sandia National Laboratories Report No. SAND95-0775, 1995. @footnote 3@M. E. Riley, Sandia National Laboratories Report No. SAND96-1948, 1996.

## Thursday Morning, November 1, 2001

#### Plasma Science Room 104 - Session PS+MS-ThM

#### **Conductor Etch and Damage**

Moderator: A.E. Wendt, University of Wisconsin, Madison

8:20am PS+MS-ThM1 An Advanced 300 mm Etcher with Tunable Plasma Source for the Etching of <0.15mm Poly-Silicon Gates, J. Holland, Applied Materials, Inc., US; M. Jain, M. Shen, N. Gani, A.M. Paterson, V. Todorov, M.S. Barnes, K. Fairbairn, Applied Materials, Inc.

The current requirements for etch performance for 300mm poly-silicon gate can only be met by providing a wide enough process window that is capable of achieving uniform etching for the variety of steps needed to complete this etch. The final dimensions of the polysilicon gate are functions of the many different etch steps, the ARC/DARC open, the mainetch , soft landing step and over-etch steps. In order to achieve < 10 nm CD range for <0.15 um polysilicon features, all of these steps need to be very uniform and the CD loss (or gain) needs to be very controllable. In this next generation 300 mm etcher, a tunable inductively coupled plasma source combined with advanced gas injection technology allows etch uniformity to be optimized for all of these different steps. Results of tuning for etch uniformity will be shown. CD control of <5 nm with a total range of 10 nm is achieved. The tunable source is also combined with a precise wafer temperature control using a dual-zone electrostatic chuck to ensure CD uniformity can be achieved across the entire diameter of the 300mm wafer. The wide process window of this etcher should be capable of addressing both current and evolving applications which require etching of multiple films with multiple etch steps involving varied process conditions.

#### 8:40am **PS+MS-ThM2 Plasma-Based Copper Etch Process - Additive Gas Effects, S. Lee<sup>1</sup>**, Y. Kuo, Texas A&M University

Copper is an ideal multilevel interconnection material for VLSIC and many other microelectronic devices. However, it is difficult to etch copper into fine lines by the conventional plasma etching method under a mild process condition such as at room temperature or without the inclusion of an extra energy source, e.g., UV, IR, or a high-density plasma source. Recently, authors reported a new plasma-based copper etching method that showed a high etch rate at room temperature using a parallel-plate electrode design.@footnote 1,2@ The success of this method relies on a novel plasma-copper reaction. Instead of removing copper compounds during the plasma processing, copper was converted into a solution soluble compound accumulated on the surface. This reaction product was subsequently removed with a HCl solution. The resulting copper pattern has a vertical profile. In this paper, we are going to discuss the additive gas (Ar, N@sub 2@, CF@sub 4@, and O@sub 2@) effects on the Cl@sub 2@ plasma-based copper reaction process. In addition to the reaction rate, the product's morphology, structure, and the undercut of the photoresist pattern have been studied. The added gas can enhance or hinder the reaction rate and the progress in the radial direction through various mechanisms. Experimental results are interpreted by the plasma phase chemistry, ion bombardment phenomena, and the original copper structure. The composition and chemical states of the reaction product are characterized by EDS and XPS. The film's morphology and structure are examined by AFM, SEM, and XRD. This study enhances our understanding of the unique plasma-based copper etching process that is critical to many microelectronic and optoelectronic applications. Authors would like to acknowledge staffs in the CIMS of Texas A&M University for AFM and XPS analyses. @FootnoteText@ @footnote 1@ Y. Kuo and S. Lee, Appl. Phys. Lett. 78, 1002, (2001) @footnote 2@ Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188, (2000).

#### 9:00am PS+MS-ThM3 Silicon Gate Etching: Potential Strategies for Future CMOS Devices, G. Cunge, L. Vallier, O. Joubert, J. Foucher, X. Detter, CNRS/LTM, France INVITED

In less than ten years CMOS devices will operate in the sub-50 nm gate length regime. The fabrication of the gate will be the key issue of the device fabrication process since the variation in gate dimension must not exceed the nominal CD targeted by few nm. In this work, some of the most promising gate strategies are investigated 1) resist mask on SiON antireflective layers versus hard mask approaches 2) standard HBr/Cl@sub2@/O@sub2@ chemistries versus CF@sub4@ (or NF@sub3@) added chemistries. The origin of CD deviation are investigated for each

single step of the different strategies: correlations between chemistry and plasma operating conditions analysed by mass spectrometry, passivation layer formation on the feature sidewalls analysed by XPS and CD deviation will be established. Our preliminary experiments show that the passivation layers formed on the mask sidewalls induce very severe CD gain during standard gate etch steps. The objective is first to minimize the CD deviation induced by each individual step of the process (by decreasing the passivation layer thickness). Ultimately, the process has to be tuned so that the CD loss or gain of each individual step compensate each other to maintain the CD in the targeted window. In final, by comparing the impact of mask materials as well as the impact of chemistries (standard or clean) on CD control, we may give some interesting conclusions on the most promising strategy. In parallel to this study, we evaluate the current strategies used to obtain gates smaller than the dimension printed by the lithography (resist trimming or "notched gate approach") and try to draw some clear conclusions on the best approach for manufacturing.

#### 9:40am PS+MS-ThM5 Sidewall Passivation Mechanism of CF@sub4@ Added Polysilicon Gate Etch Process, T. Lill, F. Ameri, S. Deshmukh, D. Podlesnik, Applied Materials; L. Vallier, O. Joubert, CNRS/LTM, France

For the traditional HBr/Cl@sub2@/O@sub2@ gate etch process, anisotropy is achieved by forming silicon, oxygen, and halogen containing compounds on the sidewall of the etching structures. These compounds inhibit the isotropic etch and are removed by from the etch front via ion sputtering and ion assisted desorption. The introduction of fluorine via CF@sub4@ to a typical HBr/Cl@sub2@/O@sub2@ polysilicon etch process suppresses the formation of SiOxBry or SiOxCly via formation of volatile SiF@sub4@. Speculations that carbon based polymers play an important role in the sidewall mechanism for the CF@sub4@ polysilicon gate etch chemistry have recently been confirmed by in-situ XPS studies in the Silicon DPS chamber at CNRS/LETI in Grenoble. In this paper we present more detailed studies of the sidewall composition for different CF@sub4@ and O@sub2@ flows. The results suggest the coexistence of silicon oxyhalogenides and carbon polymers on the sidewall for theHBr/Cl@sub2@/CF@sub4@/O@sub2@ gas mixture. The carbon content in the sidewall passivation layer increases strongly when the oxygen flow is reduced. The XPS results will be correlated with findings on chamber wall condition (oxide or carbon mode), change of the critical dimension for dense and isolated lines during gate etching (critical dimension microloading), and etch rate differences between doped and undoped polysilicon. We will present experimental line width data that corroborate the idea of change in sidewall passivation from compounds that are formed on the etching surface (silicon oxyhalogenides) to compounds formed in the gas phase (carbon polymers) when CF@sub4@ is added to the plasma. Typically, profile and critical dimension microloading are significantly reduced for the CF@sub4@ added chemistry as a result of the change in the sidewall passivation mechanism. The superior etch performance and the increased productivity due to clean chamber walls explain the rapid acceptance of this polysilicon gate etch chemistry in high volume VLSI production.

#### 10:00am PS+MS-ThM6 Manufacturing Viability of the "Notched Gate" Process for sub 0.1µm Technologies, J. Foucher<sup>2</sup>, L. Vallier, G. Cunge, O. Joubert, CNRS/LTM, France; T. Lill, Applied Materials

The development of new integrated circuit generations, at a unique rate in the semiconductor history, imposes the development of new technologies. Recently, Integrated Circuit manufacturers have evaluated new strategies to make gate transistors smaller than the resolution allowed by the lithographic tool available for manufacturing. One of them is to decrease the resist feature dimension before gate etching (resist trimming), the other approach is to design a "notched gate" etch process with a controlled etch rate of silicon in the lateral direction (the bottom of the gate is smaller than its top). We first describe in details the main differences between a notched gate process and a standard gate etch process and introduce the notion of passivation layer engineering. We demonstrate that when the process is accurately tuned, gate dimension of 10 nm can be obtained on a 200 mm diameter wafer. We mainly concentrate on several aspects of the process which determine its industrial viability: - What are the plasma operating conditions and chemistry required to stabilize a "notched gate" process or in other words what are the impact of the wall conditions on notch reproducibility ? - Can we solve the CD control issues of the notched gate process ? We will present experimental data demonstrating clearly that the notch depth rate is strongly dependent on the gate environment. In other words, the lateral etch rate which controls the notch depth is

<sup>1</sup> **PSTD Coburn-Winters Student Award Finalist** *Thursday Morning, November 1, 2001*  <sup>2</sup> PSTD Coburn-Winters Student Award Finalist

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aspect ratio dependent and impacted by the plasma non-uniformity. In conclusion, we clearly demonstrate the strong limitations of the notched gate process for manufacturing.

10:20am PS+MS-ThM7 Properties of Pulsed ICPs with rf Substrate Biases@footnote 1@, P. Subramonium, M.J. Kushner, University of Illinois Pulsed inductively coupled plasmas (P-ICPs) are of interest for controlling reactive fluxes to the substrate in microelectronics fabrication. In particular, negative ion fluxes to the wafer can be obtained in electronegative pulsed plasmas. In order to achieve anisotropy of the fluxes, rf substrate biases must also be used with P-ICPs. This is problematic since the increase in plasma potential obtained with an rf bias tends to trap negative ions. A moderately parallel implementation of the 2-dimensional Hybrid Plasma Equipment Model (HPEM) was used to investigate P-ICPs in electronegative gas mixtures having continuous and pulsed rf substrate biases. Electron properties are obtained using a Monte Carlo Simulation. In Cl@sub 2@ at 10 mTorr (PRF=10 kHz, duty cycle 50%), the electron temperature, after falling in the first part of the afterglow, increases in the late afterglow signifying a transition to a capacitive mode. The onset of the increase in T@sub e@ comes earlier with increasing rf bias voltage. The increase can be attributed to progressively larger rates of sheath heating resulting from the decreasing electron density, increasing sheath width and increasing sheath speed. Coincident with the increase in T@sub e@ comes an increase in sheath potential which prevents negative ions from escaping from the plasma. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

### 10:40am PS+MS-ThM8 Magnetic Field Effects and Electron Shading Damage, W.W. Dostalik, Texas Instruments, Inc.

The use of magnetically enhanced plasma etch systems (MERIE) is widespread in semiconductor manufacturing. A primary concern with such systems is the risk of plasma process induced damage. In this paper, we discuss several of the candidate mechanisms in which magnetic fields may affect plasma damage associated with the electron shading effect (ESE). In particular, we consider for the case of a permanent magnet MERIE reactor the effects of guiding center drifts (e.g., gradient drift and curvature drift) on charged particle fluxes, of magnetic field effects on individual trajectories, and of non-uniformity in a typical magnetic field map. These effects are calculated in a two-step fashion. In the first step, an experimentally measured magnetic field map of a commercial plasma reactor is input into a computer program that calculates the various drift velocities and non-uniformity for typical plasma parameters. In the second step, the results of these calculations are used to affect incoming charged particle fluxes in local scale Monte Carlo simulations including the magnetic field and local topography. Charge accumulation and the resulting Fowler-Nordheim injection current are accounted for in the Monte Carlo simulations.

11:00am PS+MS-ThM9 Effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar Plasma on III-V Compound Semiconductor Devices, B. Luo, University of Florida; K. Ip, Agere Systems; F. Ren, K.P. Lee, S.J. Pearton, C.R. Abernathy, University of Florida; R.J. Shul, Sandia National Laboratories; S.N.G. Chu, Agere Systems; C.W. Tu, University of California, San Diego; C.S. Wu, Win Semiconductor; K.D. Mackenzie, Unaxis USA Inc.; C.H. Hsu, Feng Chia University, Taiwan

The effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar plasma exposures on the dc and rf characteristics of pseudomorphic AlGaAs/InGaAs high electron mobility transistors (HEMTs), GaAs metal semiconductor field effect transistors (MESFETs), and AlGaAs/GaAs heterojunction bipolar transistors (HBTs) were investigated. The experiments were conducted in a Plasma Therm 790 inductively coupled plasma (ICP) system. The influences of rf chuck power(10-100W), ICP source power(100-800W), chamber pressure(2-10mtorr) and durations(10-240sec) on device performance were studied. To analyze the rf results, a device equivalent circuit model was proposed to realize damage effects on the transistor small-signal elements. Several plasma damage mechanisms were identified for the degradations of device dc and rf characteristics, including creation of surface and bulk deep level recombination centers, preferential loss of As atom from the surface due to energetic ion bombardment and passivation of Si donors by formation of Si-H and Si-D neutral complexes. Auger and atomic force microscopy (AFM) were also used to characterize the atomic ratio and roughness of plasma damaged surface, respectively.

11:40am PS+MS-ThM11 Plasma Induced Physical Damage and Contamination on the SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Film after Etching in Cl@sub 2@/CF@sub 4@/Ar Plasma, D.P. Kim, C.I. Kim, Chung-Ang University, Korea; W.J. Lee, B.G. Yu, ETRI, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) have been developed as dielectric materials of capacitor. To fabricate high density FRAM, plasma etching is indispensable process for the anisotropic pattern definition because it has good selectivity and excellent process control. However, the detrimental impact of plasma etching process on device characteristics has been existed. As feature size decreases, the plasma induced damages can decrease the performance of device. The plasma induced damages can be broadly classified as residue contamination, plasma-caused species permeation, bonding disruption and current flow damage. Etching mechanism and damages on SBT thin film during etching process have less reported in the literature. SBT thin films were etched in Cl@sub 2@/CF@sub 4@/Ar plasmas with measuring etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The maximum etch rate was 1060 Å/min in Cl@sub 2@(10)/CF@sub 4@(20)/Ar(80). The small addition of Cl@sub 2@ into CF@sub 4@(20)/Ar(80) plasma will decrease the fluorine radicals and the increase Cl radical. The etch profile of SBT thin films in Cl@sub 2@/ CF@sub 4@/Ar plasma is over 80°. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to investigate the surface morphology of SBT thin films exposed in plasma. High-resolution transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS) and x-ray diffraction (XRD) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current and hysteresys loop of Pt/SBT/Pt capacitor. From the results, damages in SBT etching was occurred in the near surface and Ar ion bombardment and nonvolatile etching by products caused to change of crystallinity and surface morphology.

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#### Plasma Science Room 104 - Session PS-ThA

**Feature Profile Evolution** 

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

#### 2:00pm PS-ThA1 Predicitve Profile Evolution Simulation in Plasma Etching, V. Vahedi, D. Cooperberg, L.B. Braly, R.A. Gottscho, Lam Research Corporation INVITED

The ability to predict feature profile evolution as a function of initial patterned profile and process set points will enable reduction in process development time and cost, speed process transfer, and inspire novel process integration approaches. Feature profile simulators have been used in prior studies to qualitatively capture the evolution of both etching and depositing processes. These simulations combined with results from molecular and/or ion beam experiments, chemical analysis of passivation and selvedge layers, plasma diagnostics of density, temperature, and composition have been used to help refine the understanding of the dominant surface mechanisms governing feature evolution and microscopic uniformity. Despite these efforts, our understanding of the complicated surface reaction mechanisms and gas phase kinetics which govern etching and/or deposition of films for commercial applications is incomplete and has prevented truly predictive profile evolution simulations. Commercial etch applications are designed for processing complex film stacks and must meet challenging specifications for mask and stop layer selectivities, sidewall-angle and/or shape, feature width, dense versus isolated feature loading, corner rounding, etch rate, uniformity, and productivity. These demands often require the use of multiple reactive process gases leading to many ion and reactive neutral species. Under these conditions, a semi-empirical approach is the most reasonable way to develop a feature evolution simulation. Our approach is to reduce the complexity of the system using a reduced set of incident species, etch and deposition mechanisms often investigated in the literature under less complex conditions where fluxes have been measured or modeled, blanket etch/deposition rates as a function of reactor settings, and a limited amount of cross-sectional SEM and Langmuir probe data to calibrate the profile simulator. In the current work, we outline a method for calibrating a semi-empirical process simulator and present simulations for Cl2/BCl3 plasma etching of resist patterned Al/0.5%Cu lines. The simulator has been used to predict feature profile evolution as a function of inductively coupled power, RF bias power, and Cl2:BCl3 flow ratio. A silicon trench isolation process simulator may also be discussed.

#### 2:40pm PS-ThA3 Investigation of Fluorocarbon PECVD from c-C4F8 for use as Passivation during Deep Silicon Etching, C.B. Labelle, V.M. Donnelly, G.R. Bogart, R.L. Opila, A.M. DeSantolo, A. Kornblit, Agere Systems

Deep silicon plasma etching is of great importance in fields such as MEMS and photonics. The most commonly used etching technique is the so-called Bosch process, where etch (SF@sub 6@/O@sub 2@) and passivation (c-C@sub 4@F@sub 8@) steps are continuously alternated to achieve vertical profiles. To investigate the passivation step, fluorocarbon films were deposited from c-C@sub 4@F@sub 8@ in a Surface Technology Systems High Rate Advanced Silicon Etch tool, which uses an inductively coupled plasma source. Film deposition rate decreases from 1000 to 740 Å/min as pressure increases from 10 to 25 mTorr, while it increases from 350 to 1500 Å/min as power increases from 300 to 1000 W. Film refractive indices (n) increase roughly linearly from 1.373 to 1.381 for the same pressure range. Carbon 1s XPS shows that, for the ranges explored, pressure and power don't significantly affect the film composition, with films generally consisting of ~ 9% CF@sub 3@, 38% CF@sub 2@, 32% CF, and 21% C-CF. The high CF@sub 2@ and CF fractions correlate with the low refractive indices observed; the slight change in n with pressure is due to replacement of CF@sub 2@ by C-CF as pressure increases. OES data indicate that the C@sub 4@F@sub 8@ is largely broken down into C@sub 2@, F, CF@sub 2@, and CF. Therefore, the films may be formed by C@sub 2@ deposition with subsequent fluorination, CF@sub x@ deposition, or a combination of both. Quadrapole mass spectrometry of the chamber effluents indicates that CF@sub 4@ (50% of effluent), C@sub 2@F@sub 4@ (25%), and C@sub 2@F@sub 6@ (14%) are created. Therefore, recombination, most likely on the walls, can generate larger C@sub x@F@sub y@ species, which also contribute to the film. The effect of residual gases from the etching step on film composition and deposition mechanisms will also be discussed.

3:00pm PS-ThA4 lons in Holes - Experimental Measurements of Ion Trajectories Inside Surface Features on rf-biased Wafers, J.R. Woodworth, Sandia National Laboratories; I.C. Abraham, Intel Corporation; P.A. Miller, R.J. Shul, B.P. Aragon, T.W. Hamilton, C.G. Willison, Sandia National Laboratories

Most microelectronic devices go though one or more stages in a plasma etching discharge in which energetic ions and radicals are used to etch deep holes or lines in the parts being fabricated. Recent computer models coupled with experimental measurements have greatly improved understanding of the bulk plasmas in these etching discharges. Comparatively little is known for certain however, about interactions between the plasma and the wafer material inside the actual features being etched. This lack of knowledge stems primarily from the absence of experimental data on plasma parameters inside the small surface features. In this talk, we will report direct measurements of ion fluxes, energy distributions, and angular distributions as a function of position at the bottom of small holes in wafers as well as near straight walls and in corners of larger wafer features. 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.

#### 3:20pm PS-ThA5 Gate Etching for ULSI Technology : Critical Dimension Control in the sub 0.1 μm Regime, X. Detter, L. Vallier, L. Cunge, O. Joubert, CNRS/LTM, France; R. Palla, I. Thomas-Boutherin, ST Microelectronics, France; T. Lill, Applied Materials

In a CMOS process, gate etching is still one of the hottest topic since the accuracy required in gate dimension control is more and more severe. Today, a gate etch process is often composed of a BARC etch step and a polysilicon main etch step, followed by a soft landing step (to preserve the gate oxide) and an overetch step. Each step is individually involved in the critical dimension (CD) control of the gate and contributes to some extent to the CD deviation. In theory, a very precise pattern transfer is possible for each step of the process if : 1) the etching is perfectly anisotropic, 2) the mask dimension is maintained intact during the process (no passivation layer deposition on the mask sidewall and no mask erosion). In practice, for each process step, etch products are deposited on the mask and on the feature sidewalls. The layer formed on the mask sidewalls generates a CD deviation whereas the passivation layer formed on the material being etched protects it against profile deformation. In this talk, a preliminary study of the CD deviation induced by each step of a polysilicon gate etch process is performed and correlated with sidewall analysis by X-ray (XPS). Standard photoelectron spectroscopy chemistries (HBr/Cl@sub2@/O@sub2@) and self clean chemistries (HBr/Cl@sub2@/O@sub2@/CF@sub4@) are compared. In final, for each process step, plasma operating conditions and chemistry are adjusted to minimize the CD deviation of the process and the most promising strategy is proposed.

#### 4:00pm **PS-ThA7 Determination of the Mechanisms Involved in the Creation of the Bowing during the Etching of Deep Anisotropic Trenches in an ICP Reactor**, *M. Boufnichel, F. Grangeon,* GREMI, CNRS-Universite d'Orleans, France; *S. Aachboun,* STMicroelectronics, Tours; *P. Lefaucheux, P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

In this study, we use a cryogenic technique instead of the polymerising one. The cryogenic method has two main advantages: it is faster and cleaner than the classical one, which uses polymerising gas such as C4F8. A cryogenic method with a SF6/O2 chemistry plasma in an Alcatel ICP (Inductively Coupled Plasma) reactor is used to achieve deep trenches with high aspect ratio (>10) and high anisotropy. The etching rate in 2 microns wide and 100 microns deep trenches is about 3.5 microns /min. The slope of the trenches can be adjusted from 88 ° to 90 ° and selectivity to oxide is higher than 300:1. However, profiles need to be improved, mainly by reducing the bowing and undercut effects. Bowing is a local lateral etching located on the side-walls and resulting in profiles destruction while undercut is a lateral silicon etching at the Si/mask interface resulting in trenches larger than the mask opening. One can notice that it is difficult to mask these defects with a cryogenic method without modifying the other features of the etching process such as the etch rate. Bowing creates the most severe damage as the change in profile slope due to bowed surfaces creating voids when it is necessary to refill the trench for a specific application. This study deals with improvements in these effects. We investigated the outcome of process parameters (pressure, bias voltage, temperature, gases flow rates) and mask characteristics (nature, thickness, side slope, trench width) in parallel with electrical and actinometrical measurements using respectively a langmuir probe and optical emission

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spectroscopy (OES). We also tested several more or less conducting masks (oxide, PSG, Aluminium,...). The different mechanisms responsible for bowing and undercut will be discussed and evaluated.

4:20pm PS-ThA8 Investigation of Plasma Etching of SiO@sub 2@ Contact Holes using a Statistical Method and a Theoretical Profile Evolution Model@footnote 1@, C. Liu, B. Abraham-Shrauner, Washington University The experimental data@footnote 2@ in the plasma etching of SiO@sub 2@ contact holes in a MERIE reactor with a CF@sub 4@/CHF@sub 3@/Ar gas mixture is analyzed by using a statistical method and our semianalytical etch profile evolution model. The experimental data is from a 2@super 5-1@ fractional factorial experiment design.@footnote 3@ The five factors which are treated as independent variables are the plasma reactor process variables: CHF@sub 3@ flow rate, CF@sub 4@ flow rate, Ar flow rate, gas pressure, and magnetic field. The DC bias voltage, the etch rate, the sidewall slope and the microtrench depth of the etch profiles are analyzed as response variables. The aim of the statistical analysis is the prediction of the measured response variables as a function of the five plasma reactor process variables. The accuracy of the predicted values of the response variables is reported. To reveal the underlying mechanism of the external processing parameter effects on the etch profiles, we simulate the SEMs etch profiles under different processing conditions using our theoretical etch profile evolution model, which is based on the calculation of particle fluxes arriving at the etching surface. Comparison between the control parameters of our model and the measured variables can give us more insights into how to control the etch rate and the etch profile. The new concept of our approach is the combination of the statistical prediction of the measured properties of the etch profile as a function of the reactor process variables and the theoretical simulation of the etch profile. @FootnoteText@ @footnote 1@This research is supported in part by the Boeing-McDonnell foundation. @footnote 2@Melisa J. Buie and Jeremiah Pender supplyed the data and SEM micrographs. @footnote 3@M. J. Buie, J. T. P. Pender, and P. L. G. Ventzek, Jpn. J. Appl. Phys. Part 1, 36(7B), 4838(1997).

#### Plasma Science Room 134/135 - Session PS-ThP

#### **Plasma Etching Poster Session**

#### PS-ThP1 Damage Recovery of Etched PZT Thin Films in CF@sub 4@/Cl@sub 2@ Plasma with the Addition of Ar, N@sub 2@ and O@sub 2@, M.G. Kang, K.T. Kim, C.I. Kim, Chung-Ang University, Korea

Ferroelctric lead zirconate titanate (Pb(Zr,Ti)O@sub 3@) thin films have been known for their applications in memory devices such as nonvolatile ferroelecric random access memory (FRAM) because of their high dielectric constants and bistable polarization. It is expected that PZT will improve the limitations in storage density encountered in conventional Si memory technology. Among the various dry etching techniques, great attention has been paid to the reactive ion etching (RIE) because it provides a high degree of anisotropy and good selectivity with the great process control. However, the RIE process degrades electrical properties, which are related to physical damage and chemical residue contamination. In this study, PZT thin films were etched by additive Ar, N@sub 2@, O@sub 2@ in CF@sub 4@/Cl@sub 2@ inductively coupled plasma. The etch rate is observed by various parameters. We also observed the effect of etching damage in PZT thin films during etching in inductively coupled plasma (ICP) etching system. SEM is used to survey the etching profile. We investigate that the recovery characteristics of etching damage used rapid thermal annealing (RTA) at various temperature. The polarization-electric field (P-E) curves were measured with a RT66A ferroelectric tester. The physical damages to the near surface of PZT are evaluated by atomic force microscopy (AFM) and x-ray diffraction (XRD) The etched surface was surveyed x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) analysis. This research was supported by the Consortium of Semiconductor Advanced Research (COSAR) as project No. 00-B6-C0-00-09-00-01

#### PS-ThP2 Dry Etching Characteristics of YMnO@sub 3@ Thin Films Using Inductive Coupled CF@sub 4@/Cl@sub 2@/Ar Plasma, C.I. Kim, D.P. Kim, Chung-Ang University, Korea

Ferroelectric YMnO@sub 3@ thin films are excellent dielectric materials for high integrated ferroelectric random access memory (FRAM). YMnO@sub 3@ thin films have one polarization axis (c-axis), contain heavy and harddeoxidizing elements, and do not contain volatile elements such as Bi and Pb, which easily diffuse into the Si substrate and lead to point defects. In this study, YMnO@sub 3@ thin films were etched with a CF@sub 4@/Cl@sub 2@/Ar gas combination in inductively coupled plasma (ICP). Etching characteristics on ferroelectric YMnO@sub 3@ thin films have been investigated in terms of etch rate and selectivity. The CF@sub 4@/(CF@sub 4@+Ar) was fixed at 0.2, and the YMnO@sub 3@ thin films were etched by adding Cl@sub 2@. Etching properties of YMnO@sub 3@ were measured according to the various etching parameters such as the rf power, dc-bias voltage, chamber pressure, and gas mixing ratio. The chemical reaction in the surface of the etched YMnO@sub 3@ films was investigated with x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). For the diagnosis of the CF@sub 4@/Cl@sub 2@/Ar plasma, optical emission spectroscopy (OES) and Langmuir probe were used. The etch profile and surface residues of etched YMnO@sub 3@ thin films was investigated by scanning electron microscopy (SEM). @FootnoteText@ Acknowledgement; University Research Program supported by Ministry of Information and Communication in South Korea.

#### PS-ThP3 Reduction of Plasma-Induced Damage through Ion-Ion Synchronous Bias, L.J. Overzet, S.K. Kanakasabapathy, University of Texas at Dallas; K.P. Cheung, M.V. Malyshev, Agere Systems

Electron-shading induced differential-charging of anisotropic etch structures has been shown to be a cause of plasma process induced-damage.@footnote 1@ It is due to a disparity in the angular velocity distributions of negative and positive species in conventional electron-ion plasmas. Electron-free plasmas, also known as negative-ion/positive-ion (ion-ion) plasmas can be made devoid of this disparity. The comparable masses and average energies of negative and positive ions in the center of an ion-ion glow allow nearly equal anisotropy to be produced in their velocity distributions when biased. Ion-ion plasmas can be formed by extinguishing the plasma power and waiting an appropriate time. For example: electrons are lost rapidly (~10's of µsec) to attachment in the afterglow of pulsed Cl@sub 2@ discharges leaving behind an ion-ion

plasma that lasts for ~100's of µsec. Alternating fluxes of high kinetic energy positive-ions and negative-ions can then be produced by applying a low-frequency AC bias to the processing substrate. When this AC bias is pulsed synchronously with the plasma power and phase locked to the ionion plasma, it can produce alternating fluxes of positive-ions (Cl@sub 2@@super +@) and negative-ions (Cl@super -@).@footnote 2@ This ionion `synchronous bias' is superior for extracting negative-ions compared to an `asynchronous bias' due to the low DC self-bias it induces. We have demonstrated a reduction in electron-shading induced potentials for ionion synchronous bias using in-situ charge-monitoring circuitry. We have also compared some cross-sectional micrographs of etched polysilicon lines on oxide. Our limited results indicated an improvement in etch profiles for ion-ion synchronous bias at the smallest linewidth of 0.45µm. @FootnoteText@ @footnote 1@ G.S. Hwang and K.P. Giapis J. Appl. Phys., 82, 566(1997) @footnote 2@ S.K. Kanakasabapathy, L.J. Overzet, V. Midha and D.J. Economou, Appl. Phys. Lett., 78, 22(2001).

# **PS-ThP4 Investigation of Nitride Morphology after Self-Aligned Contact Etch, D. Keil**, J.W. Shon, B.A. Helmer, T. Chien, P. Gopaladasu, Lam Research Corporation; J. Kim, Samsung Corporation, Korea; H. Hwang, NASA Ames Research Center

Self-Aligned Contact (SAC) etch has emerged as a key enabling technology for the fabrication of very large-scale memory devices. However, this is also a very challenging technology to implement from an etch viewpoint. The issues that arise range from poor oxide etch selectivity to nitride to problems with post etch nitride surface morphology. Unfortunately, the mechanisms that drive nitride loss and surface behavior remain poorly understood. Using a simple langumuir site balance model, SAC nitride etch simulations have been performed and compared to actual etched results. This approach permits the study of various etch mechanisms that may play a role in determining nitride loss and surface morphology. Particle trajectories and fluxes are computed using Monte-Carlo techniques and initial data obtained from double Langmuir probe measurements. Etched surface advancement is implemented using a shock tracking algorithm. Sticking coefficients and etch yields are adjusted to obtain the best agreement between actual etched results and simulated profiles.

# **PS-ThP5 Development of Self-aligned Contact Technology on a Capacitively Coupled System**, *T. Chien*, *C. Nelson*, *D. Keil*, *E.A. Hudson*, *K. Makhratechev*, Lam Research Corporation

Self-aligned contact (SAC) technology was developed to enable efficient reduction of active areas of an integrated circuit. However, implementation of SAC etch and process integration has been very challenging. Many factors are known to influence SAC etch performance. This work addresses the effects of the machine factors (pressure, gas flow/ratio, temperature, RF powers, other gas addition, etc.) and different fluorocarbon gases in a capacitively coupled plasma etch system. Results from several designed experiments (DOE's) will be present which explore main effects and interactions for several key variables affecting SAC etch. Trends identified include critical dependencies of etch results on power and gas flow. To better understand the mechanisms responsible for the trends observed, UV absorption spectroscopy and Langmuir probe measurements were also implemented for each DOE condition. Correlations observed between these measurements and etch trends will be discussed.

#### PS-ThP6 Surface Analysis of a High Selective Polysilicon to Oxide Plasma Etching Process, *T. Tai, S. Molis, W. Yan,* IBM, SRDC

With continuing reduction of minimum feature size in semiconductor device fabrication, limited gate stack height becomes necessary to control the bitline?wordline capacitance, and to reduce bitline contact aspect ratio for better process performance. Tungsten, which has a lower sheet resistance and hence the capability to reduce gate stack height, has been selected to replace widely used tungsten silicide in the gate structure. However; because of the chemical nature of tungsten, tungsten to oxide RIE selectivity in the Fluorine etching enviroment is not adequate to prevent thin gate oxide (less than 40A) to be punched through. A polysilicon etch step with adequate selectivity to oxide has been developed to prevent gate oxide punchthrough. Xray Photoelectron spectroscopy and Time-of-Flight Secondary Ion mass spectrometry were applied to investigate the Poly and Oxides in a high-density plasma etching environments with HBr/Cl2/O2 chemistry. The results will lead to the undertanding of the RIE chemistry that provide the selectivity.

PS-ThP7 Investigation of the Performance of MERIE Etcher for Extended Conditions of Consumable Upper Electrode/Gas Distribution Plate Lifetime, D.V. Semach, Silicon Manufacturing Partners Pte. Ltd., Singapore Lifetime of consumable parts used in semiconductor industry correlates directly with cost-of-ownership and overall equipment effectiveness. In this study lifetime of Bush upper electrode that is the consumable part of TEL85DRM dielectric etch chamber had been improved from conventional 500 to 1200 RF hours. The part is produced of aluminum, anodized and equipped with inserts gas holes been drilled through. During processing gas holes are enlarged because of the inserts material etching hence the gas distribution pattern conductance is increased. Continuously monitoring equipment and process parameters (process gases partial pressure, particle count, etch rate, non-uniformity, etching profile, etc.) subject to the gas holes integrated size there had been found that the pattern conductance increasing up to 400 % (during the part operation from 500 to 1200 RF hours) and even by 40 times (as a result of special inserts boring) had not affected these parameters. It proves that the pattern conductance is not a limitation factor for the chamber performance and plasma is stable and uniform under these conditions. As is well known, during running and wet clean the surfaces of the chamber parts deteriorate progressively. Series of chemical analysis of polymeric stratums been peeled out from the electrode surface had shown significant increase of AL and O level at the stratum side being in contact with the surface with increasing of the part operational time. However surface analysis of wafers been processed after the chamber wet clean and seasoning had not disclosed any AL and the other metal contaminations as at the initial stage as at 1200 RF hours of the part operation. All the results had been confirmed for several electrodes and chambers. The real possibility to extend the part lifetime to 2000 RF hours and more if apply soft wet clean method detailed in the body has also been shown.

#### **PS-ThP8 Electron-Temperature Control in 915 MHz ECR Plasma**, *N. Itagaki*, Kyushu University, Japan; *S. Kawakami*, *N. Ishii*, Tokyo Electron Co. Ltd., Japan; *Y. Kawai*, Kyushu University, Japan

In semiconductor processing, it is required to control the electron temperature in plasma for progress of microelectronic devices and minimization of substrate damage. Since the reactive processes occurred strongly depend on the electron temperature, this control is also necessary to find the best conditions for various plasma processings. An electron cyclotron resonance (ECR) plasma source has attracted much attention for its high electron density (10@super 17@-10@super 18@ m@super -3@) that can be achieved at low gas pressure (10@super -4@-10@super -3@ Torr). However, in a conventional ECR plasma produced by 2.45 GHz microwave, the electron temperature is relatively high, and it is quite hard to control the electron temperature in a wide range. Recently, we succeeded in production of a low-electron-temperature ECR plasma with high electron density using 915 MHz microwave. Furthermore, it was found that the electron temperature depends on the external conditions such as incident microwave power, gas pressure and magnetic field configuration. In this report, we measured the electron temperature of 915 MHz ECR plasma in detail and attempted to control the electron temperature by changing the external conditions. As a result, it was found that the electron temperature of the 915 MHz ECR plasma can be easily controlled by changing the incident microwave power in the case that the magnetic field configuration is flat. Especially, at the gas pressure of 8.5 mTorr, the electron temperature decreased nearly from 7 eV to 1.6 eV as the microwave power was decreased from 2.5 kW to 0.5 kW. In addition, we have tried to investigate the mechanism of a low-electron-temperature plasma production with 915 MHz microwave by measuring the spatial profile of the plasma parameters and wave patterns.

# PS-ThP9 High Performance SiO@sub 2@ Etching using C@sub 4@F@sub8@ and C@sub 5@F@sub8@, S.H. Rha, D. You, C.W. Lee, J.Y. Choi, Advanced Technology Line, Korea

SiO@sub 2@ etching characteristics of C@sub 4@F@sub 8@ and C@sub 5@F@sub 8@ were comparatively studied. The 2MHz rf-biased electrostatic chuck in13.56MHz high-density transformer coupled plasma (TCP) reactor was used. The typical operating conditions is 10-15 mTorr, 300-400 sccm(total flow rate), 2500W Source power and 1800W rf-bias power. C@sub 4@F@sub 8@ and C@sub 5@F@sub 8@ were employed as source gases to investigate their differences in etching performance and selectivity on both SiO@sub 2@ and PR. For increasing the SiO@sub 2@/PR Selectivity. The CH@sub 2@F@sub 2@ was used. And the optimum CH@sub 2@F@sub 2@ mixing ratio for SiO2 etching is reported that. Based on these results, in sub-micron contact hole(0.1-1µm) etching, we

achieved SiO@sub 2@ etch rate is more than 6000A and SiO@sub 2@/PR selectivity is 5:1.

PS-ThP10 Applicability of a Hollow-electrode Plasma Jet System for Etching of Diamond-like Carbon (DLC) Films, P.E. Lima, H.S. Maciel, M. Massi, Instituto Tecnologico de Aeronautica - ITA, Brazil; R.D. Mansano, LSI - Escola Politecnica - USP, Brazil; G. Petraconi, W. Urruchi, C. Otani, Instituto Tecnologico de Aeronautica - ITA, Brazil

Partly in response to the challenges of etching high-aspect-ratio features, it is introduced a new plasma tool based on the hollow-electrode discharge. Plasma jets are capable of operating at relatively low gas pressures, 10@super -5@ Torr, what is in somehow advantageous in comparison with reactive ion etching (RIE) systems, because it reduces contamination from sputtered electrode materials, which eventually produces undesirable micromasks. On the other hand, the non-uniformity of the etching with plasma jets limits the applicability of this technique for microelectronic purposes. To minimize this problem, a plasma beam formed by a multi hollow-electrode system was developed in order to produce an uniform beam, which was used to etch diamond-like carbon (DLC) films. These films of approximately 1.5 µm thick were deposited on 3-inch diameter, p-type, (100) silicon wafers, by magnetron sputtering, at a deposition rate of approximately 4.5 nm/min. After being characterized, samples were separated in two batches, one of then was etched in a single hollowelectrode plasma jet and the other one was etched in a multi hollowelectrode plasma jet. During the etch processes a mechanical mask was used to cover part of the samples with the purpose of producing a step between the etched and non-etched regions. This step was measured by a perfilometer and the etch rates were determined in different positions on the samples. The results obtained with the single configuration showed a high non-uniformity in the etching. This non-uniformity was substantially reduced by using the multi hollow cathode system. The multi hollowelectrode plasma beam system revealed to be a reliable technique for DLC films processing, giving etching uniformity and etching rate characteristics as good as those obtained with usual RIE systems, with the advantage of being a simple and low cost equipment.

#### PS-ThP11 Influence of Polymerization on Pressure Control System Performance during Dielectric Etch Processes, D.V. Semach, Silicon Manufacturing Partners Pte. Ltd., Singapore

Various effects taking place in plasma etch systems exert essential influence upon process characteristics and control. In this study pressure control valve (PCV) operation during dielectric etch processes in MERIE (magnetically enhanced reactive ion etching) reactor was investigated. Growth of polymers on grating type baffle separating plasma and exhaust zones of the reactor is causing the exhaust conductance and in this connection chamber pressure to change dynamically. During running of an evaluated process based on increased gas flow of high-molecular fluorocarbon and argon mixture fast changes in PCV behavior were observed. Intensive polymerization was suspected to be a main reason for these changes. Detailed monitoring of chamber manometer and PCV readings let to evaluate polymers rates of growth and shrinkage and dynamics of some other processes affecting the valve movement, and also define the limitations for pressure control. The polymers formed on anodized aluminum chamber parts were found to be thick, very dense and hard. Detailed examinations of the polymeric stratums showed that they consisted of many thin layers. The thickness of one layer was just about a hundred nanometers. Thus we could suppose that every single layer of formed polymer refers to individual wafer. Chemical analysis of the polymers showed that they consist mostly of fluorine and carbon. Ratio of fluorine to carbon contents was about 2 to 1. The investigation results show that polymers formed during plasma etching may significantly decrease pumping and pressure control systems capability depending on temperature, structure, density and volume of the polymers. Process pressure, mass flow of gas mixture components and correlation between RF power on and RF power off time intervals were found to be the main factors responsible for polymers formation and behavior.

PS-ThP13 Challenges in 0.1µm Line and Space Nitride Hard Mask Etching, Y.S. Chae, J. Kim, Samsung Semiconductor R&D Center, Korea; W.M. Ahn, J.W. Shon, Lam Research Corporation; W.S. Lee, I.S. Kim, Y. Kang, Samsung Semiconductor R&D Center, Korea; J.P. Lee, B.K. Kong, Lam Research Corporation; C.J. Kang, J.T Moon, Samsung Semiconductor R&D Center, Korea

As device feature size shrinks near 0.1 micron, PR (Photo Resist) erosion, microloading and striation are all much more serious due to 3D effect. And the thickness of nitride hard mask also becomes higher to prevent the

electric short between gate and contact during SAC (Self Aligned Contact) process. These lead to require PR selectivity higher up to 4. Since the vertical metal-etch traditionally produces positive CD (Critical Dimension) bias, the nitride hard mask etching needs to produce negative CD bias. Therefore, we need to etch PR with high selectivity and negative CD bias, which is in trade-off relations. We have characterized the process trends in CD bias, striation and PR selectivity of nitride hard mask etching in terms of additive chemistry, RF power and its ratio. Best process results show narrow process window for relatively lower power with narrow range of O2 flow. Successful results for 0.09 micron process are obtained for lower ion energy process with high Ar flow.

#### PS-ThP14 Trench Etch Characteristics of Via-first Dual Damascene Process on 0.15µm SRAM Technology., W.-S. Kim, Hynix Semiconductor Inc., South Korea, Korea; J.-I. Cho, I.-S. Choi, J.-J. Lee, H.-S. Shin, H.-S. Yang, Hynix Semiconductor Inc., South Korea

Recently, via-first dual damascene process with cost-effectiveness and fabrication complexity reduction has been proposed as an alternative to get over the limitation of conventional interconnection processes. However, it has some problems such as the formation of the fence and the facet around the via hole in the trench etching process. Especially, the fence can cause bad via hole filling and the incomplete removal of resist residues. In this study, we investigated the effect of CH2F2 and CO addition into C4F8 plasma on fence formation, and also relationship between organic ARC fill thickness and fence formation. Physical features were analyzed with SEM and TEM. And electrical characteristics were examined with continuity/bridge patterns. For the surface analysis, the etched oxide films with C4F8/CH2F2 and C4F8/CO, respectively, were characterized with XPS. In the trench etching with C4F8/CH2F2 plasma, the fence height was increased with organic ARC thickness. Since the organic ARC on the sidewall of the via hole played a role as the etch barrier during trench etching. fence-shaped oxide residue was occurred around the via hole. Moreover, in this study, we could also observe the fence profile in a condition of no organic ARC with C4F8/CH2F2 plasma because the polymer deposited at the top edge of the via hole prevented oxide etching around the via hole whereas fence free with C4F8/CO plasma. The XPS surface analysis data clearly showed that C4F8/CH2F2 plasma had higher intensity for C-C bonds and C-H bonds in comparison with C4F8/CO plasma. Therefore, in order to obtain fence-free trench profiles, optimization of ARC thickness and also use of low polymerizing plasma were simultaneously needed. Consequently, for 0.15µm SRAM technology, the fence-free trench etching was achieved with low polymerizing C4F8/CO plasma and optimum ARC fill thickness which was slightly lower than the etch stopper in the via hole.

#### PS-ThP15 Etching Characteristics for Porous Silica (k=1.5) by Using NLD Plasma in a Low Pressure, Y. Morikawa, N. Mizutani, T. Hayashi, ULVAC Japan Ltd., Japan; T. Uchida, ULVAC Japan Ltd.

The etched profile of the porous silica@footnote 1@ (produced in ULVAC Japan Ltd.) was obtained as an almost vertical structure. The etch rate was approximately 2 times higher than that of the SiO@sub 2@ film when linear saturated perfluoro carbon compounds were used,@footnote 2@ because the overall film density of the porous silica is low. However, in the case of C@sub 4@F@sub 8@ (Octafluorocyclobutane) plasma, the etch rate ratio to the SiO@sub 2@ was about 1.45. When C@sub 4@F@sub 6@ (CF@sub 2@=CFCF=CF@sub 2@: Hexafluorobutadiene) was used, the etch rate ratio was also very low (0.6). So the etch rate strongly depends on the gas structure, whereas the SiO@sub 2@ etch rate is almost constant. The Vpp of the RF bias was almost same for all kind of fluorocarbon gases. It was observed that CxFy@super +@ ions were main species in the C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@ plasma (QMS) and a polymer film was formed on the etched surface (XPS). Therefore, it is considered that the fluorocarbon polymer formed in the pore suppresses the etch rate of the porous silica in the C@sub 4@F@sub 8@ or C@sub 4@F@sub 6@ plasmas. C@sub 3@F@sub 7@I (CF@sub 3@CFICF@sub 3@: 2iodoheptafluoropropane) gas was examined. The etch rate selectivity of photo resist to porous silica went up about 50%, compared with C@sub 3@F@sub 8@. Negative F@super -@ ion in the C@sub 3@F@sub 7@I plasma was obtained as a very small peak, contrary in the C@sub 3@F@sub 8@ and other fluorocarbon plasmas. On the other hand, I@super -@ ion intensity was very strong. These results may imply that the iodine in the plasma plays some roles for etching. @FootnoteText@ @footnote 1@C. Tanaka and H. Murakami, Extended abstract (The 61st Autumn Meeting, 2000); The Japan Society of Applied Physics, 750 (4a-P4-27). @footnote 2@Y.Morikawa et al., J.Vac.Sci.Technol.A19(4), Jul/Aug (2001).

PS-ThP16 Trench Etch Challenges in a Cu/Low-k Via-First Dual Damascene Scheme, P. Jiang, H. Hong, Q. Hong, K.J. Newton, Texas Instruments, Inc. In a via-first copper dual damascene integration scheme, trench patterning is one of the most critical steps, for both lithography and etch. Due to via topography, resist thinning occurs in dense via region during trench pattern, resulting in potential resist breakdown during trench etch. To prevent trench bridging or metal shorting, it becomes necessary to keep good trench etch profile and high resist selectivity. However, another key issue for trench etch is oxide ridge formation around vias which can disrupt metallic barrier and copper deposition resulting in degraded device reliability. In achieving good trench profile and high resist selectivity, oxide ridges often become severe. Therefore, it is very challenging to control profile, resist selectivity and oxide ridge formation simultaneously. In this paper, we will discuss the options and results that meet the special requirements for Cu/low-k dual damascene trench etch. The low-k dielectric film used in this work was an organosilicate glass (OSG). The effect of etch process parameters on trench profile, resist selectivity and ridge formation will be discussed, along with the resist effect on resist etch selectivity. Electrical results showing significant yield improvement with the optimal etch process will also be reported.

#### PS-ThP17 N@sub 2@ Addition Effect on Highly Accurate Organic Low-k Etching Process, Y. Morikawa, ULVAC JAPAN Ltd., Japan; M. Ozawa, N. Mizutzni, ULVAC JAPAN Ltd.; T. Hayashi, ULVAC JAPAN Ltd., Japan; T. Uchida, ULVAC JAPAN Ltd.

Etchings for organic low-k materials, FLARE@super TM@ and SiLK@super TM@, had been carried out at a N@sub 2@ dominant mixing ratio in an N@sub 2@ + H@sub 2@ plasma generated by the magnetic neutral loop discharge (NLD) method at low-pressure below 1 Pa.@footnote 1@. We had tried to control micro-trench free profile by using nitrogen-organic surface reactions in a fine pattern etch process. As the result, we were able to successfully control the profiles without micro-trench when the substrate temperature was kept above 0°C, blow 1 pa. Usually, when the N@sub 2@ + H@sub 2@ plasma with H@sub 2@ dominant mixing ratio or only NH@sub 3@ plasma is used, bowing profiles were obtained such a substrate temperature. However, the plasma with the N@sub 2@ dominant mixing ratio was used, bowing did not occur in the temperature range of 0°C to 30°C. Under this condition, the N1s/C1s ratio on the etched surface increased with increase of the temperature. This may be due to an enhancement of nitrogen addition reactions on the surface and thereby the sidewall is passivated. Negative ions in the H@sub 2@+N@sub 2@ plasma were measured by using a quadrupole mass spectrometer. NH@sub 2@@super -@ and CN@super -@ negative ions were observed as main peaks. These species decreased with the pressure. The CN@super -@ ion signal abruptly decreased at the end point. We will also report a finely deep etching process over 1.0 µm without any micro trench and without pillar residues on the etched surfaces. @FootnoteText@@footnote 1@Y. Morikawa et al, Proc.Symp.Dry Process, 263 (2000) @footnote 2@Y. Morikawa et al, J.Vac.Sci.Technol., A19 (4), Jul/Aug (2000).

#### PS-ThP18 Damage Free Gate Shrinkage Method Using Low Temperature Si@sub 3@N@sub 4@ Film Deposition and SF@sub 6@/O@sub 2@ Gas Mixture Etching, C.R. LIM, J.H Shin, LG-Elite (LG-Electronics Institute of Technology), South Korea

Recently, the concern about sub micron gate length formation method for development of high performance FET is increasing. But, sub micron gate length could not be gotten using optical contact aligner or cheap stepper machine. And, in order to reduce resistance in FET gate electrode which had short gate length, we use normally T-shaped gate whose head was wide about 1 micrometer. In our lab, we tried to make FET whose gate length was shorter than the exposed gate length. After lithography of about 0.4 micrometer gate length using stepper, and we deposited silicon nitride film at low temperature to protect photo resist from deformation and at low work pressure to form conformal shape. Deposited silicon nitride film was etched using conventional RIE medium-pressure reactor and we tried to find proper etch condition from varied SF@sub 6@/O@sub 2@ gas ratio and could know proper etch condition of the ratio 3:7 at work pressure 100mTorr and RF power of 100watt. Doing so, we could get FET which has gate length of 0.1 micrometer and the deposition and etching condition harm no damage on wafer surface. In order to find low temperature silicon nitride film deposition condition and directional etching condition, we used SEM, optical emission spectroscopy and dielectric constant measurements.

PS-ThP19 A Study on the Polymer Residues Formation at the Via-hole and its Removal by Remote Oxygen/Nitrogen and Hydrogen Plasma, *S.B. Kim, H. Soh, Y. Kim, Y.C. Kim, H. Jeon,* Hanyang University, Korea

For multilevel device fabrication, via-holes are generally dry etched for electrical connection between the upper and lower metal layers.@footnote 1@ The ashing and photo resist (PR) strip processes are generally followed to remove the PR and polymerized residues, respectively.@footnote 2@ However, the PR strip is the wet chemical process and causes environmental problems. In this study, low temperature remote plasma dry cleaning process that removes both the PR and polymer residues containing carbon and fluorine will be described. The radio frequency remote oxygen/nitrogen plasma was used to remove the PR and polymer residues simultaneously. The cleaning efficiency was systematically evaluated at various conditions such as the oxygen and nitrogen ratio, plasma power, exposure time, gas flow rate and sample temperature. The hydrogen plasma treatment was also carried out to remove polymerized residues formed at the bottom nitride layer oxygen/nitrogen plasma cleaning. In-situ Auger electron microscopy, X-ray photoelectron spectroscopy, atomic force microscope analysis systems were used to evaluate the cleaning effects and to avoid recontamination such as carbon absorption in the air. Scanning electron microscope provided a preliminary assessment of cleaning performance. Preliminary results indicated that the hydrogen plasma treatment subsequent to oxygen/nitrogen PR ashing process was very efficient to remove the polymerized residues formed at the bottom nitride. @FootnoteText@ @footnote 1@D. Louis, E. Lajoinie, W. Mun Lee, D. Holmes, Microelectronic Engineering, 41/42, 377-382 (1998) @footnote 2@Ying Wang, Sandra W. Graham, Lap Chan, SheauTan Loong, Journal of Electrochemical Society, 144, 1522-1528 (1997)

## PS-ThP20 Studies on Photoresist Etching in Inductively Coupled Plasmas, X. Xu, P. Shoenborn, LSI Logic

Bottom anti-reflective coatings (BARCs) are now used in applications such as gate patterning that requires the tight critical dimension (CD) control. BARC removal must be accomplished before the film (e.g. poly and dielectric) is etched. BARC etch is a critical step that can affect the final line width of the etched features. In general, an oxygen plasma with additives is used to etch BARC, in which photoresist has been trimmed simultaneously. In this work, the effect of O@sub 2@/N@sub 2@ and O@sub 2@/He plasmas on etching of photoresist is investigated on Lam TCP 9400PTX system. The self-bias voltage on the wafer has been measured for a variety of conditions with different top source powers, bottom bias powers, gas mixtures and gas flow rates. The results show that compared to O@sub 2@/N@sub 2@ plasma, the self-bias voltage is lower and the etching rate of resist is higher for O@sub 2@/He. Our measurements indicate that the etched products can lead to an increase of self-bias voltage with a fixed bias power. The influence of etched products is due to the decrease of the ion flux to wafers, which is shown through the use of plasma simulator, the Hybrid Plasma Equipment Model (HPEM).

#### PS-ThP21 Method to Prevent Notching in Polysilicon Gate Etch Process with Long Over-Etch, W. Pau, M. Shen, Applied Materials

In this study, we investigate the factors that can prevent notching in polysilicon gate etch process with very long over-etch. Conventionally, process optimization focuses on varying the parameters in over-etch to prevent notching. The effect of main etch and the interactions of main etch and over-etch are often overlooked. This paper explores the effect of main etch as well as the coupling between main etch and over-etch in notching elimination. The process consists of a timed main etch 1 (ME1) with CF@sub4@/Cl@sub2@/N@sub2@ chemistry followed by а HBr/Cl@sub2@/He-O@sub2@ main etch 2 (ME2) step . Then a high selectivity over-etch (OE) step uses HBr/He-O@sub2@ to etch any remaining polysilicon residue. ME2 matrix results reveal that this step plays a significant role in notching prevention. For ME2 step, a high pressure, high bias power, high HBr/Cl@sub2@ ratio and high He-O@sub2@ flow are most effective in preventing notching. For OE step, low pressure, low He-O@sub2@ flow and low source power are most effective in prevent notching. There are two main mechanisms that are responsible for notching prevention in ME2: (1) profile modification through ME2 and OE interaction and (2) sidewall passivation enhancement by ME2 only. High pressure in ME2 prevents notching through the first mechanism by having a taper profile after ME2 endpoint. This profile is then modified by OE so that a vertical profile is achieved. The effect of bias power in notching reduction, on the other hand, is attributed to the second mechanism. High bias power densifies the sidewall passivation to provide better protection at the bottom of the film, thus preventing notching.

PS-ThP23 Chemical Mechanisms of the Etching and Non-etching of Magnetic Materials in CO/NH@sub 3@ Plasmas, A.S. Orland, Auburn University; *R. Blumenthal*, Auburn University, usa

The etching of Fe, Ni and Co foils in CO/NH@sub 3@ plasmas have been investigated using supersonic pulse plasma sampling mass spectrometry. It has been previously reported@footnote 1@ that plasmas based on high mole fractions of CO are observed to result in the deposition of carbide films, while pure NH@sub 3@ plasmas and high NH@sub 3@ content mixtures are reported to etch the metals, with a maximum etch rate of 500A/min at ~ 13% CO in NH@sub 3@. Mass spectra were collected over the entire range of composition from 100% CO to 100% NH@sub 3@ plasmas. In pure CO plasmas, the major plasma products that were observed are CO@sub 2@, C@sub 2@O@sub 2@, C@sub 2@O@sub 3@ and C@sub 3@O@sub 2@. The addition of NH@sub 3@ to the feed gas results in a complete elimination of the C@sub 3@O@sub 2@ species at ~60% CO, while C@sub 2@O@sub 3@ persists to ~40% CO. As the C@sub 3@O@sub 2@ and C@sub 2@O@sub 3@ disappear, a series of peaks around N@sub 4@H@sub 6@ appears. The CO@sub 2@ signal initially decreases rapidly as the CO composition is lowered to ~60%, and then remains relatively constant until disappearing completely in the 100% NH@sub 3@ plasma. The C@sub 2@O@sub 2@ species, believed to be a weakly bound dimer, is the only product that shows a smooth transition to nitrogen containing analogs as the NH@sub 3@ percentage increases. C@sub 3@O@sub 2@ is well-know to act as a carbon atom donor, through successive losses of CO, and consequently, it is concluded that this species is responsible for the deposition of the carbide layer that inhibits the etching of metals in pure CO plasmas. The rapid suppression of the chemical sequence responsible for forming this species, as NH@sub 3@ is added, makes etching possible for higher fractions of NH@sub 3@ in the plasma. @FootnoteText@ @footnote 1@ K.B. Jung, et al. J. Vac. Sci. Technol. A 17(2), 535 (1999)

PS-ThP24 Resist Trimming Process Using High Density Plasma for Sub-0.1µm MOSFET, C.Y. Sin, B.H. Chen, National University of Singapore; K. Loh, P. Yelehanka, Chartered Semiconductor Manufacturing, Singapore

Because of the resolution limit of the 248nm lithography and immaturity of the 193nm lithography process, resist trimming process using oxygen containing gas mixture has been developed for sub-0.1@micro@m MOSFET fabrication. In this paper, the characteristics of resists trimming in high-density plasma were investigated. Experimental results are presented to show the trimming behavior of resist as a function of RF source power, bias power, temperature, linewidth to space ratio, gas composition and reactor pressure. Effect of gas composition on trimming process were evaluated using three different gas mixtures: HBr/O@sub 2@ and Cl@sub 2@/O@sub 2@ as well as CF@sub 4@/O@sub 2@. The gas mixture of CF@sub 4@/O@sub 2@ gives high trim, improved resist sidewall roughness and good uniformity. Studies of X-ray photoelectron spectroscopy (XPS) will be performed to determine the chemical composition of the resist sidewall passivation. The features studied comprised of alternate polysilicon lines and spaces. The amount trimmed is linearly proportional to trim time. For resist trimming, the experimental results revealed that the trimming process is of very feature density dependence. rim rate is dependent on linewidth to space ratio, but is independent of initial linewidth for the same linewidth to space ratio. Trim rate increases at low CF@sub 4@ gas flow ratio and then decreases. Trim rate of 0.66@micro@m/min can be achieved. The activation energies of trimming for dense and isolated line are found to be 0.13eV and 0.128eV, respectively, at gas composition of 100sccm CF@sub 4@/30sccm O@sub 2@ but have guite different pre-exponential constants, which suggests to be feature density dependence. Bias power has no significant effect on trim rate. Reactor pressure in the range from 5mTorr to 20mTorr also does not affect much the trim rate. The resist trimming process is found to be reproducible and controllable, making it a useful process for nanometerscale device fabrication.

#### PS-ThP25 The Geometric and Chemical Effect of Polymer Deposition and Etch-product Redeposition on the Etching of SiO@sub 2@ Trench Sidewall in a CF@sub 4@ Plasma, J.H. Min, S.W. Hwang, G.R. Lee, S.H. Moon, Seoul National University, Korea

The effect of etch-product redeposition on the etching of SiO@sub 2@ trench sidewall in a CF@sub 4@ plasma was studied using a Faraday cage with a slit on the upper plane located in a transformer coupled plasma reactor. The Faraday cage with a slit allowed ions to be injected vertically on the specified portion of SiO@sub 2@ bottom surface under the practical plasma condition. The effect of the bottom surface on the redeposition of the etch products on the sidewall was studied by comparing the properties

of the sidewall surfaces obtained with or without the etch-product emission from the bottom surface. The trench bottom was etched at the bias voltage ranging between -200 and -600V and at the source power between 200 and 600W. The bias voltage and the source power had complex influences on the redeposition of the etch products on the sidewall because they changed the concentration of radicals, and the flux and the energy of ions injected on the bottom surface. Specifically, the bias voltage increased the redeposition rate mostly by physical sputtering, while the source power increased the rate mostly by chemical sputtering. The concentration of CF@sub 2@ and F radicals increased with the bias voltage and the source power, which enhanced the polymer deposition on the sidewall. The shape of the Si-O peak in the Infrared(IR) spectrum of the redeposition film was similar to that of thermal oxide, but the Auger Emission Spectroscopy(AES) indicated that the O/Si ratio was higher for the redepsition film than for the thermal oxide. Analyses of the sidewall surface by AES and IR indicated that F radicals reacted with the oxide layer to break the Si-O bond. In the case of oxygen addition, the etch rate of the bottom surface increased but the rates of redeposition and polymer deposition on the sidewall decreased due to the enhanced production of F radicals in the plasma.

#### PS-ThP26 Evaluation of High Temperature Process in W/poly Si Gate Stack Etching in a Dual Frequency Plasma Reactor, J. Hong, Samsung Electronics, Korea, South Korea; J.S. Jeon, C.J. Kang, Samsung Electronics, Korea

W/poly Si stack becomes potential candidate in giga bit DRAM gate structure due to its lower sheet resistance compared to WSi/poly Si stack. Emerging process issues in W gate module are high etch selectivity of W over Si@sub 3@N@sub 4@ mask and poly Si stack down for self aligned contact scheme. High temperature process was evaluated in W etching to achieve high etch selectivity based on Cl@sub 2@/O@sub 2@ gas chemistry in a dual frequency plasma reactor. Mask loss and W profile were found to be strong function of gas ratio, process pressure and ion energy. The presence of oxygen inhibited Si@sub 3@N@sub 4@ mask loss by oxidation while enhancing W etching at high process temperature (150°C). Two steps W etch was developed in order to reduce the recess of poly Si in W overetch step. Poly Si recess showed a different behavior with Cl@sub 2@/O@sub 2@/NF@sub 3@ based gas chemistry at the temperature raging from 100°C to 150°C. Recess was optimized at 120°C at the expense of mask loss and W profile. Conventional HBr based chemistry appeared to have inability to provide sidewall passivation in poly Si etching at high temperature. Gas chemistry for sidewall passivation and high selectivity over gate oxide at high temperature will be discussed.

#### PS-ThP27 The Effect of Reflected Ions on the Etching of Silicon Dioxide Surface in the Fluorocarbon Plasma, *G.R. Lee*, *S.H. Hwang*, *J.H. Min*, *S.H. Moon*, Seoul National University, Korea

In the plasma etching process, ions reflected from the sidewall surface of a deep, narrow pattern contribute to the additional etching of the other surfaces, which may be called as a secondary etching. When the aspect ratio of the etched pattern becomes high, the influence of the secondary etching on the etch profile becomes significant. In spite of its importance, however, the secondary etching due to the reflected ions has not been studied much especially under the conditions of industrial plasma processes. In many cases of the etch-profile simulation, it has been commonly assumed that ions reflect from the sidewall in an elasticspecular mode, particularly when the ion-incident angle is high. In this study, we observed the position and the extent of the secondary etching of silicon dioxide in a fluorocarbon plasma due to the reflected ions with various incident angles. The ion angles were controlled by using a Faraday cage and specially fabricated sample holders placed in a plasma reactor. The experimental results deviated from those predicted based on an elastic-specular assumption when the ion-incident angles were close to 90°. According to the analysis of the substrate surface after the plasma etching, the deviation of the ion reflection from the elastic-specular mode originated from the deposition of a fluorocarbon film on the substrate surface. The film-deposited surface became rough, and consequently ions reflected from the surface in a non-elastic, non-specular mode.

**PS-ThP28 Effect of Ion Bombardment on Developed Photoresist Morphology during Reactive Etch Processes for sub 0.25 micron Semiconductor Devices,** *M. Naeem, R. Wise,* IBM Microelectronics Division; *F. Wang,* Cypress Semiconductors; *G. Worth, D. Dobuzinsky,* IBM Microelectronics Division; *Z. Lu,* Infineon Technologies; *A. Hadi,* Conexant The use of advanced resist systems has become necessary for lithography in processing of advanced (sub 0.25 µm) semiconductor devices to achieve acceptable image quality. These novel resist systems are more sensitive to both post exposure treatments as well as the ion bombardment component present in reactive ion etch (RIE) processes. We discuss the impact of resist interactions with low energy plasma and morphological changes in the resist profile. In particular, the effects of different photoresist constituents, post develop bake conditions, various RIE steps and RIE parameters in capacitively coupled plasma (CCP), magnetically enhanced RIE (MERIE) and inductively coupled plasma (ICP) systems on resist morphology and the quality of final etched images are presented.

PS-ThP29 Study on the Low Angle Forward Reflected Neutral Beam Etching System, *D.H. Lee*, Sungkyunkwan University, Korea; *J.W. Bae*, Sungkyunkwan University, Korea, South Korea; *S.D. Park, G.Y. Yeom*, Sungkyunkwan University, Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuit. However, plasma etching could give serious disadvantages due to the energetic charged particles generated in the plasma which cause radiation damage such as physical defect, increased gate oxide breakdown, charging, etc. To avoid these charge-related and physical impact-related damages, several low-damage processes have been proposed. One possible alternative to avoid these problems is a low energy neutral beam etching. In this study, neutral beam has been generated using a low angle forward reflected neutral beam and its characteristics such as the degree of neutralization, etch characteristics, etc. have been studied as a possible anisotropic etching technique without charging. When the reactive ion beam was reflected on a reflector at the angles lower than 15°, most of the ions reflected were neutralized and also the lower reflector angle showed the higher degree of neutralization. Complete removal of the ions in the reflected beam could be accomplished by installing a retarding grid system between the sample and the reflector and by applying a potential higher than the maximum ion energy of the flux. This reflected neutral beam source has been devised to be scaleable to a large diameter and also to etch polymer and SiO@sub 2@ anisotropically. In order to obtain a large flux from the ion source, inductively coupled plasma was used as the plasma source and specially prepared extraction grids which have very dense and small holes were used. Details of the developed neutral beam source and its properties will be discussed in addition to the etch characteristics obtained using the low angle reflected neutral beam source.

# PS-ThP30 Highly Selective Etching of Al/AIN Structures for Metallization of SAW Devices, *F. Engelmark*, *I.V. Katardjiev*, *G.F. Iriarte*, Uppsala University, Sweden

Metallization is a critical step in the fabrication of high frequency thin AIN film based SAW devices. Both state-of-the-art lithography as well as high selectivity and anisotropy during etching of Al with respect to AIN are required for low loss and high performance devices. In this work, the etch rates of reactively sputtered AIN, sputtered AI, thermal SiO@sub 2@ and Shipley 1813 photo resist as well as the selectivity between Al/AIN, Al/SiO@sub 2@ and resist/Al have been systematically studied during ICP RIE. Emphasis is focused on obtaining high Al etch rates, while at the same time keeping the etch rate of AIN and that of the resist sufficiently low. High anisotropy is obtained by passivating the sidewalls by the addition of oxygen. The recipe developed is based on a modified Al etch using a mixture of BCl@sub 3@, Cl@sub 2@, O@sub 2@ and Ar. The parameters varied were gas composition, process pressure, substrate bias and ICP power. Generally it is found that the Al etch rate exhibits a maximum with the O@sub 2@ flow, while the AIN etch rate decreases monotonically. Substrate bias is found also to be an important parameter with respect to both etch rates and selectivity. At optimized conditions (500 W ICP power, 35 W chuck power, 50 sccm BCl@sub 3@, 25 sccm Cl@sub 2@, 10 sccm O@sub 2@, 0 sccm Ar, pressure 10 mTorr) the Al etch rate is 1700 nm/min with a selectivity of 58 towards AIN and 10 towards the resist. The same recipe, slightly modified, has also shown similar AI etch rates when etching Al over SiO@sub 2@ with a selectivity of up to 180. High anisotropy of the Al etch rate is observed with increasing O@sub 2@ flow. The former has been determined from cross-sectional SEM observations.

PS-ThP31 W/WNx/Dual-Poly Stack Gate Etching for 0.15 μm Tech. Full CMOS SRAM, B.-K. Lee, Y.-J. Choi, I.-K. Yang, I.-S. Seo, H.-S. Shin, H.-S. Yang, Hynix Semiconductor Inc., South Korea

As SRAM cell composed of pMOS and nMOS is scaled down to deep submicron regime, the surface channel pMOS with p+ poly Si gate is a key technology to realize high performance full CMOS SRAM device, because of its strong immunity to short channel effect. Another important issue to be considered with scaling down of the device is reduction of resistance-

capacitance delay along channel width. The W/WNx/Dual-Poly stackedgate electrode is promising method for these requirements. In the present study, we investigated the effect of gas chemistry on the W/WNx etching characteristics such as profile angle, surface morphology of poly Si and selectivity of the W/WNx over SiON hard mask and poly Si, respectively. Physical features were analyzed with SEM and TEM, and electrical properties were measured. The surface analysis of etched W/WNx film with XPS and plasma analysis with L/P(Langmuir Probe), OES(Optical Emission Spectroscopy), RGA(Residual Gas Analysis), and Posi-SIMS were also performed. When Cl2 was added to NF3, the laternal etching in W/WNx was suppressed due to increase of polymerization. In addition, the selectivity of the W/WNx over SiON was improved by the increase in etch rate of W/WNx and also the decrease in that of SiON induced from the change of plasma state. In case of Ar and O2 addition, the selectivity of W/WNx over poly Si was increased, and consequently sublayer poly Si loss was reduced during over etching. Finally, the addition of CF4 to NF3 made the surface morphology of poly Si smooth resulting from more uniform W/WNx etching during the over etching. On the basis of these results, W/WNx/Dual Poly stack gate etch process having a vertical profile, no sub Si attack and no residue could be achieved with NF3/Cl2/CF4/O2 gas for W/WNx etch and with HBr/Cl2/O2 gas for poly Si etch for 0.15 Tech. SRAM and beyond. Keywords: etching, tungsten, dual gate, SRAM, surface channel pMOS.

#### PS-ThP32 Trimming Photoresist in a DPS(TM)II 300mm Poly Etch System -Control of Trimming Rate, Uniformity and Stability, *M. Shen*, *O. Yauw*, *N. Gani*, *C. Lin*, *Y. Lai*, *M. Chu*, Applied Materials

As the IC industry aggressively moving towards 0.10um gate length devices, requirements on CD control become increasingly difficulty to meet. Resolving 0.10 um line width with great accuracy and uniformity on 300 mm wafer is a major challenger for conventional photolithography technology. Therefore, trimming photoresist through etching has become a very attractive alternative to speed up the road map towards 0.10um technology using existing photolithography. Resist trimming, however, requires strict control of trimming rate, uniformity and stability. Trimming linearity is another important element for precise CD control. With integrated CD metrology approach, it is possible to adjust the trimming time based on in-coming wafer to obtain desired final CD for each wafer. The study presented here outlines some of the development works for resist trimming process on Applied Materials DSP(TM)II 300mm poly etcher system. Trimming up to 30nm with less than 5nm in range uniformity has been achieved on 300mm wafers. Excellent CD uniformity controls on overall process involving trimming, hardmask and polysilicon gate were demonstrated on DPS(TM)II 300 system.

# PS-ThP33 Effects of Gas Chemistry of Inductively Coupled Plasmas on the Multi-Layer Gate Metal Etching Characteristics for TFT-LCD Devices, Y.J. Lee, Sungkyunkwan University, Korea, South Korea; C.H. Yi, B.K. Song, M.J. Chung, Sungkyunkwan University, Korea; M.P. Hong, Samsung Semiconductors, Korea; G.Y. Yeom, Sungkyunkwan University, Korea

For advanced TFT-LCD manufacturing processes more conductive gate materials are required for the next generation large size and the high quality of thin film transistor liquid crystal displays (TFT-LCDs). For gate metal layer, single gate metals such as Al-Nd and Ag, and double gate metals such as Al-(Cr, Mo, MoW, or W) are widely studied. Currently, the patterning of gate metals is done by wet etching methods. With the wet etching method, however, the tapered patterning of Al-alloy mentioned above is nearly impossible. Also, most of the capacitively coupled RIE-type equipments available for FPD devices are suffered from relatively low plasma densities, therefore, low etch rates. Therefore, in this study, the tapered etching of multi-layer gate metals such as Ag, Al-Nd, and double gate metal films (Al-Cr, Mo, W, or MoW) deposited on glass substrates were studied using high density inductively coupled plasmas (ICP) and the etch characteristics were investigated as a function of gas combination, pressure, dc self-bias voltage, and inductive power. Chlorine and brominebased gas were used with N@SUB 2@, O@SUB 2@, and Ar as additive functional gases. Depending on the materials, the different etch rates were obtained for the same process parameter condition. For example, the etch rates close to 1500Å/min could be obtained using BCl@SUB 3@/HBr chemistry for Al-Nd etching and the etch selectivity over photoresist was close to 1. The low etch rates were attributed to the Nd in Al. Using the plasma diagnostic tools such as optical emission spectroscopy and quadruple mass spectroscopy, the etching mechanisms of various gate metal layers with these chemistries were investigated. Variations of surface composition for various gas mixtures were also investigated using X-ray

photoelectron spectroscopy. The etch profiles and surface defects were observed with a scanning electron microscope.

# PS-ThP34 The Influence of Ar Flow Rate on Photoresist Selectivity in High Density Plasma Etching of SiO@sub2@, E. Haikata, S. Sasaki, T. Yoshida, K. Nojiri, Lam Research Co., Ltd, Japan

As dimension of LSI becomes smaller, higher photoresist selectivity to SiO@sub2@ is required in high-aspect-ratio contact hole etching, because photoresist mask becomes thinner to get enough resolution. Although C@sub4@F@sub8@/Ar/O@sub2@ gas chemistry is widely used for SiO@sub2@ etching, the influence of Ar flow rate on photoresist selectivity is not clear. This paper presents the influence of Ar flow rate on photoresist selectivity and etching profile along with the discussion on the basis of XPS and OES analysis. In the experiment, Ar flow rate was changed from 50 sccm to 500 sccm in Transformer Coupled Plasma Etcher, with C@sub4@F@sub8@/O@sub2@ flow rate kept constant. With increasing Ar flow rate, photoresist selectivity increased because the photoresist etch rate decreased drastically, while the SiO@sub2@ etch rate decreased only slightly. In contrast, at low Ar flow rate, photoresist selectivity dropped remarkably at small diameter holes due to RIE Lag, and etch stop was observed. XPS data showed that polymer deposited on the photoresist at high Ar flow rate contained more C-C and C-CF@subx@ chain, and it was more C rich. From OES results, C@sub2@/CF@sub2@ ratio increased as Ar flow rate increased. Since C radical has higher sticking coefficient than CF@sub2@ radical, C is thought to deposit at the upper part of the contact hole and photoresist surface, leading to higher selectivity because C rich polymer has high resistance to plasma attack.On the other hand, CF@sub2@ is thought to go into inside of the hole, causing etch stop at low Ar flow rate. We conclude that high Ar flow rate has advantage of wider etch stop margin and higher photoresist selectivity.

#### PS-ThP35 Novel Organic Low-k Dielectric Etching by Using CH@sub 3@NH@sub 2@ / N@sub 2@ Plasma, H. Nakagawa, Matsushita Electric Co., Ltd., Japan; Y. Morikawa, T. Hayashi, ULVAC JAPAN Ltd., Japan

A Novel organic low-k etching has been developed by using a new gas chemistry of CH@sub 3@NH@sub 2@ / N@sub 2@ in a neutral loop discharge (NLD) plasma system. The organic low-k etching produces normal taper profile, no micro-trench, and small hard-mask erosion, which required for fabricating Cu / organic low-k damascene multilevel interconnects. The concept of etching is to introduce C-H passivation film with appropriate thickness on sidewall and bottom of etched patterns, and employing CH@sub 3@NH@sub 2@ / N@sub 2@ has led to the achievement of the required performance. Furthermore, we can control the taper angle of the etched profile by changing a flow ratio of CH@sub 3@NH@sub 2@ / N@sub 2@ and N@sub 2@ in this chemistry. We have already reported that the via hole etching with normal taper profile, no micro-trench and small hard-mask erosion is obtained by using a gas mixture of CH@sub 4@ / N@sub 2@ in neutral loop discharge (NLD) plasma.@Footnote 1@ In this chemistry, we were able to obtain only slight taper angle and small etch rate of photo-resist (PR) mask. The organic lowk etching by CH@sub 3@NH@sub 2@ / N@sub 2@ plasma, however, has also overcome the problems which were not achievable in the etching by CH@sub 4@ / N@sub 2@ plasma. In this presentation, we will discuss the concept of etching gas chemistry design and the etching mechanism on the basis of both QMS measurement results of plasma gas phase and composition evaluation results of the deposition film formed on the Si wafer surface during etching. @FootnoteText@@footnote 1@ H. Nakagawa et al, Tech. Dig. of Dry Process Symposium, Tokyo, 257 (2000).

PS-ThP36 Low Temperature Etch Characteristics Using 193 nm ArF Photoresist Below 0.1µm Device, W.S. Lee, Samsung Electronics, South Korea; J.W. Shon, B.K. Kong, Lam Research Corporation; J. Kim, Samsung Electronics, South Korea, Korea; E.S. Chae, Samsung Electronics, South Korea

Patterning sub 0.1 micron devices require a photoresist (PR) that is extremely photosensitive to short wavelength such as 193 nm ArF PR. However, etch problems associated with ArF PR includes higher etch rate, less selectivity, less PR thickness due to increasing opacity at shorter wavelength. For a nitride hard mask etching, process results are sensitive to process temperature. SEM pictures obtained from hard mask open process show notable improvements at -20°C. Wafer temperature measurements suggest that bulk wafer temperature is only about 10°C higher that chiller temperature. However, surface of PR could heat up to much higher than that of bulk wafer temperature, which could cause PR deformation.

**PS-ThP37 0.1µm Line and Space Nitride Hard Mask Open Process Using Ar/C@sub 2@F@sub 6@/O@sub 2@ Plasma**, *W.S. Lee*, Samsung Electronics; *J.W. Shon, B.K. Kong, E.A. Hudson*, Lam Research Corporation Traditional line and space nitride hard mask open process uses Ar/CF4/CHF3/O2 recipes. The process chemistry using both CF4 and CHF3 combination provides excellent CD control with controllable amount of polymer needed for 0.14 micron and larger devices. However, as the feature size shrinks to 0.1 micron, better PR selectivity and CD control are required. Using C2F6 based recipe, we can double PR selectivity with minimum penalty in CD blow out. We have developed C2F6 based nitride hard mask open recipe in comparison to the baseline CF4 recipe. PR selectivity and profile are much better compared to CF4 based recipes. We are reporting process trends for C2F6 based line and space nitride hard mask open process with respect to total power, power ratio, effects of adding polymerizing gas, and striation issues.

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#### Plasma Science Room 104 - Session PS-FrM

#### **Diagnostics III**

**Moderator:** M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

#### 8:20am PS-FrM1 Optical Diagnostics of Charged Particles in Processing Plasmas, A. Kono, Nagoya University, Japan INVITED

Behaviors of electrons and negative ions in low-pressure high-density inductively coupled plasmas have been studied using non-intrusive optical diagnostic techniques. An efficient multichannel laser Thomson scattering measurement system, which is highly resistant to Rayleigh scattering interference, was developed and used to study electron energy distribution functions (EEDFs). In measurements of C@sub 4@F@sub 8@/Ar plasma at a total pressure of 25 mTorr, non-Maxwellian EEDFs were observed, in contrast to Maxwellian EEDF observed for pure Ar plasma. A particle simulation suggests that the observed EEDFs result from local electron heating and subsequent cooling of electrons by inelastic collisions in the non-heating region. Laser photodetachment technique in combination with millimeter-wave Fabry-Perot resonance technique was used to study negative ion density. Measurements of CF@sub 4@/, C@sub 4@F@sub 8@/, SF@sub 6@/, and NF@sub 3@/Ar plasmas at 25 mTorr show that at an Ar dilution ratio as high as 95% and at electron densities around 10@super 11@ cm@super -3@, the negative ion density is higher than or nearly as high as the electron density. This indicates that in high-density C@sub 4@F@sub 8@, SF@sub 6@, and NF@sub 3@ plasmas electron attachment occurs as effectively as in low-density plasmas with low dissociation degrees of the feedstock gases; on the other hand, in highdensity CF@sub 4@ plasma, electron attachment takes place much more effectively than in low-density plasma, suggesting that dissociation of CF@sub 4@ results in production of highly electron-attaching species.

#### 9:00am PS-FrM3 Measurements of the Spatiotemporal Variation of Ion Flux in Plasma Etching Reactors, *T.-W. Kim, S.J. Ullal, E.S. Aydil,* University of California, Santa Barbara

Variation of the ion flux and its spatial distribution across the wafer is critical in plasma etching: ion flux uniformity at the wafer determines the uniformity of etching. Most ion flux uniformity measurements to date have concentrated on studying the radial uniformity on a plane above the wafer. There are very few ion flux measurements on the plane of the wafer, especially in two dimensions. We have designed, built, and used planar Langmuir probes and probe arrays consisting of 10-30 probes on 75 mm and 200 mm diameter wafers to measure the variation of ion bombardment flux and its spatiotemporal distribution at the plane of the wafer in two different inductively coupled plasma reactors. Twodimensional variation of the ion flux as a function of radial and angular positions on the plane of the wafer was mapped by interpolating between the probes. We demonstrate the uitility of these probes in studying factors that affect the ion flux and its uniformity including instabilities in an Ar discharge and effects of etching products in Cl@sub 2@ etching of Si. For example, in one of the reactors in Ar plasma at high pressure, a region of high ion flux ("hot spot") developes at the edge of the wafer at seemingly random positions and this "hot spot" rotates and moves around the edge on a time scale that depends on the plasma conditions. During etching of Si in a chlorine plasma, ion flux increases as a function of exposure time to the chlorine discharge and saturates on a time scale that is on the order of a few minutes. Through other diagnostic methods, this reproducible transient in the ion flux is related to the release of etching reaction products such as SiCl@sub x@ and subsequent deposition of a silicon oxychloride film on the reactor walls. Removal of this film from the wall with an SF@sub 6@ discharge resets the reactor walls back to a reproducible condition and returns the ion flux to the same level as at the beginning of the etching process.

9:20am PS-FrM4 Time-resolved Radical Measurements in a Remote Silane Plasma Using the Cavity Ringdown Absorption Technique, J.P.M. Hoefnagels, A.E.E. Stevens, Eindhoven University of Technology, The Netherlands; W.M.M. Kessels, D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

The highly sensitive cavity ringdown spectroscopy technique (CRDS) has been used for the determination of the density and plasma chemistry of SiH@sub x@ radicals in our remote silane plasma, which is used for high

rate deposition of a-Si:H and µc-Si:H. Recently, a new CRDS based technique has been developed for measuring time-resolved radical densities (@tau@-CRDS) to obtain further insight into the dynamics of SiH@sub x@ radicals and to study the interaction of these radicals with the depositing surface. In @tau@-CRDS, the plasma is modulated and the corresponding response of the SiH@sub x@ radical density is monitored by sampling the SiH@sub x@ density at various times. For this measurement, a "state of the art" data acquisition system (100 MHz, 12 bit) has been developed such that single CRDS transients can be handled up to a repetition rate of 2 kHz. It will be shown that single transient handling improves the signal-to-noise ratio drastically, even for conventional CRDS measurements. The modulation of the plasma is done by application of pulsed rf power to the substrate holder in addition to the regularly operating remote plasma. This creates only a minor additional SiH@sub x@ radical density. In this way, gas phase and surface reactivities of the species are obtained under steady state plasma operation conditions. The feasibility of the @tau@-CRDS technique has been proven on SiH radicals probing the A@super 2@@DELTA@<-X@super 2@@PI@ electronic transition at ~413 nm. By using different modulation frequencies the measurements have also revealed that a previously unidentified broadband absorption on this wavelength is due to a rather unreactive species created in the silane plasma. Furthermore, @tau@-CRDS measurements on Si and SiH@sub 3@ will be presented and the gas phase and surface reactivity of these species will be discussed on the basis of a model.

9:40am PS-FrM5 Temporally Resolved Measurement of Electron Temperature, Relative Electron Density, and Atomic Fluorine Density during Fluorocarbon/Rare-gas Plasma Etching of SiO@sub 2@, using Optical Emission Spectroscopy, *M.J. Schabel*, Bell Laboratories, Lucent Technologies; V.M. Donnelly, W.W. Tai, A. Kornblit, Agere Systems

Measuring the time-resolved behavior of processing plasmas is important for determining process end-points, tool health and process faults. One commonly used approach is to monitor the optical emission for changes that correlate conditions. Recently, we have demonstrated that the plasma emission may also be used to characterize the time-averaged behavior of fundamental plasma properties, including electron temperature (T@sub e@), relative electron density (n@sub e@) and fluorine atom concentration (n@sub F@), through the application of advanced optical emission spectroscopy. Here we have used trace rare gas optical emission spectroscopy and rare gas actinometry to measure T@sub e@, n@sub e@, and n@sub F@ at ~2 second increments in an inductively-coupled commercial plasma reactor. The temporal behavior was evaluated over a complete plasma process cycle, which included plasma strike, stabilization, chamber seasoning, silicon dioxide etch, and an oxygen chamber clean and photoresist strip. Run to run repeatability of T@sub e@, n@sub e@, n@sub F@, and O-atom density was evaluated for each step in the cycle. T@sub e@ was found to be repeatable to within  $\pm 0.5$  eV for constant step conditions. The silicon dioxide etch step, comprised of C@sub 2@F@sub 6@, C@sub 4@F@sub 8@, a carrier gas, and a trace rare gas mixture (equal parts He, Ne, Ar, Kr, and Xe), was evaluated over variations in pressure (10-90 mTorr), flowrate (120-600 sccm), and carrier gas composition (0-100% Ar, balance Ne). Corresponding measurements of etch rates and sidewall angles were found to range between 2-12 kÅ/min and 85-90°, respectively. Correlations between plasma operating conditions, fundamental plasma parameters, and etch performance will be presented.

10:00am PS-FrM6 Characterization of Mass-Filtered CF@sub x@@super +@ Ion Beams for Surface Studies of Etching, *M.J. Gordon*, California Institute of Technology; *K.P. Giapis*, California Institute of Technology, U. S. A.

Many ion beam systems used to probe plasma-surface interactions during etching are unable to deliver the tunable energy and high particle flux conditions that are typical of realistic processing plasmas. Some of the problems include inefficient ion production, space charge spreading of the beam resulting in very low fluxes, and a fixed plasma potential that requires the sample to be offset from ground in order to vary the beam energy. Furthermore, mass-filtering of the ion beam is required if the reaction dynamics of specific plasma species are to be understood. To create an improved ion source for etching studies, we have developed a mass-filtered ion beam system based on extraction of ions from an inductively coupled plasma (ICP) discharge. In our system, ions are extracted from an ICP discharge (13.56 MHz) using an accel-decel lens arrangement and injected into a transport line floating at -15 kV. The ion beam is mass filtered at high voltage using a magnetic sector, focused, and then decelerated to impinge on a grounded sample. Similar to biasing a

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wafer, capacitively coupled RF (15-30 MHz) from an auxiliary electrode is used to vary the ICP plasma potential and hence, vary the ion beam energy. Mass-filtered ion currents after focusing that approach 1 mA/cm@super 2@ can be obtained due to high ion densities in the ICP and beam transport at high voltage to avoid space charge spreading. This talk will focus on ion source design and beam characterization experiments for CF@sub x@@super +@ species extracted from ICP etching plasmas. The dependence of CF@sub 2@@super +@/CF@sub 3@@super +@ beam currents and ion energy distribution functions (IEDF's) on plasma pressure (1-10 mT) and RF inductive power (50-500W) were measured using a hemispherical energy analyzer located downstream of the sector magnet. In addition, the effect of capacitive RF bias power and frequency (15-30 MHz) on the plasma potential was investigated by monitoring the shift in the beam IEDF.

# 10:20am PS-FrM7 Ion Energy Measurements in a Pulsed Plasma with a High-resolution, Submicron, Retarding Field Analyzer, M.G. Blain, M.J. Sowa, R.L. Jarecki, Sandia National Laboratories

A silicon wafer-based, submicron, high-resolution, retarding field analyzer (RFA)@footnote 1@ was used to measure ion energy distributions in an inductively coupled plasma where the source power was pulsed on and off. Experiments were conducted in argon at pressures from 1.5 - 40 mTorr, with various source rf powers, for periods of 10-40  $\mu sec$  with duty factors from 20%-80%. In contrast to the single peak obtained with continuous Ar plasmas, distinct high and low ion energy peaks were frequently observable in the pulsed plasmas. These distinct peaks can be attributed to contributions from a high T@sub e@ inductively-powered plasma, and a low T@sub e@ afterglow, respectively. A simulation based on the global plasma model of Ashida, et al.@footnote 2@ was able to capture the qualitative trends in the pulsed data, confirming this interpretation. Additional pulsed experiments were performed with 0-100% O@sub 2@/Ar mixtures, as well as various Cl@sub 2@/Ar mixtures. Oxygen addition, in particular, produces an increased spread between the high and low energy peaks, perhaps due to depletion of electron density by attachment during the afterglow.@footnote 3@ @FootnoteText@ @footnote 1@M.G. Blain, J.E. Stevens, J.R. Woodworth, Appl. Phys. Lett., v.75, n.25, p.3923, 1999. @footnote 2@S. Ashida, C. Lee, and M. A. Lieberman, J. Vac. Sci. Technol. A, v.13, n.5, p.2498, 1995. @footnote 3@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 PS-FrM9 Characteristics of the LAPPS Ion Flux to an RF Biased Surface, D.D. Blackwell, S.G. Walton, D. Leonhardt, D.P. Murphy, R.F. Fernsler, R.A. Meger, US Naval Research Laboratory

The ion flux properties are possibly the most critical parameters in a process plasma. Every industrial plasma process, from sputtering to deposition, is highly dependent on the density, energy, and composition of the ions. At NRL, we have been experimenting with electron-beam produced plasmas as an alternative to radiofrequency (RF) driven discharges. The most promising of these sources is the hollow cathode driven Large Area Plasma Processing System. This source is designed to produce large area (> 1 m@super 2@), high density, uniform sheets of plasma. In this presentation we will show measurements of the ion energy distribution function (IEDF) from continuous and pulsed electron beam plasmas produced in 20-30 wide, 1 cm thick sheets by a 2 kV hollow cathode. The IEDF is obtained using a gridded energy analyzer incorporated into a RF biasable stage. The surface flux and IEDF in the presence of large RF voltages applied to the stage will be presented. We will also be comparing the IEDF's taken in a pulsed system and a continuous current system during the "beam on" and afterglow periods to observe their temporal evolution. Typical operating conditions are 15-20 millitorr of argon, oxygen, or nitrogen, and 150-200 Gauss magnetic field.

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