Monday Morning, November 4, 2002

Plasma Science
Room: C-105 - Session PS-MoM

Conductor Etch I
Moderator: S. Han, University of New Mexico

8:20am **PS-MoM1 The Evolution of Plasma Etching in Integrated Circuit Manufacturing**, ***J.W. Coburn***, University of California, Berkeley **INVITED**

Anisotropic plasma etching methods were introduced into semiconductor manufacturing in the late 1970s. The notion of using reactive gas glow discharges to etch solid materials had been described much earlier but it was not until the mid 1970s that the anisotropic etching capabilities of plasma etching were recognized. At this time, it was understood that the requirements for anisotropic etching were both energetic ion bombardment of the surface being etched and an exothermic chemical reaction between the gas phase reactants and the surface that form a volatile reaction product. Early plasma etching systems were primarily capacitively coupled, single frequency diodes with either planar or cylindrical geometry. In order to achieve the desired etch rates, relatively high energy (0.5 to 1 keV) ion bombardment of the surface being etched was required. However this bombardment tended to reduce etch selectivities and increase wafer damage. Furthermore, the plasma potential in capacitively coupled systems can exceed 100 volts, resulting in high energy ion bombardment and sputtering of grounded surfaces; a possible source of wafer contamination. These issues were addressed by separating the plasma generation from the wafer bias. During the early 1980s, single frequency and dual frequency triodes were popular. Later in the 1980s, inductively coupled and wave-generated plasma sources were introduced. These sources allowed the generation of high density plasmas (10^{11} to 10^{13} electrons/cm^3) which, when combined with a relatively low power capacitively coupled chuck, allowed high etch rates to be achieved with relatively low ion energies (50 - 200 eV). Today, each wafer is exposed to a plasma etching environment between 10 and 20 times during its manufacture and without the highly anisotropic etching provided by this critical process, high density IC manufacturing would not be possible.

9:00am **PS-MoM3 Resist Transformation under High Density Plasma Exposure**, ***E. Pargon***, *J. Foucher, J. Detter, L. Vallier, G. Cunge, O. Joubert*, CNRS/LTM, France, *Th. Lill*, Applied Materials

We are now entering in the development of sub 0.1 µm Integrated Circuits device fabrication where a very accurate control and understanding of plasma processes is essential to address the road map requirements. In particular, plasma processes involved in gate stack processes need special attention since several steps such as resist trimming, hard mask opening and silicon etching impact the final gate dimension. In any of these processes, the etching behaviour of photoresist exposed to the plasma plays a key role. In this study, we have performed chemical topography analyses using XPS to explore the chemical nature and thickness of the reactive layers formed on the resist patterns. XPS analyses show that the resist transformation during the resist trimming process is well correlated with the trim rate measured in HBr/O_2 and $HBr/Cl_2/O_2$ /CF_4 chemistry. In particular, a decrease in trim rate obtained when increasing the bias power is well correlated with a thicker perturbed layer formed on the resist sidewalls. A good correlation between reactive layer thickness on the sidewalls and decrease in trim rate is also observed with CF_4 addition. CF_4 based plasmas used for hard mask opening generate reactive layers as thick as 10 nm on the resist sidewalls (through the formation of a CFx-based layer). This layer is suspected to generate a loss of CD control during hard mask patterning. Deep transformations of the resist during silicon gate etching are also observed. XPS studies show that the resist mask strongly loads chlorine species as compared to an oxide hard mask and that thick passivation layers are formed on the resist sidewalls using $HBr/Cl_2/O_2$ and $HBr/Cl_2/O_2/CF_4$ chemistries. Correlations between resist behaviour and process control (mainly CD control) can be established

9:20am **PS-MoM4 A Novel Gate-Electrode Fabricating Technique using a Sequential UHF-ECR Plasma Process**, ***M. Mori***, Hitachi, Ltd.,Japan, *T. Tsutsumi*, Hitachi High-Technologies Corp.,Japan, *N. Itabashi*, *M. Izawa*, Hitachi, Ltd.,Japan

For fabricating beyond 90 nm-node devices, ArF lithography will be increasingly used. This process demands that the gate electrode must be trimmed more than 50 nm after lithography and critical dimension (CD) shift variation must be suppressed within 3-5 nm across the wafer. However, gate-electrode trimming of more than 50 nm using only ArF trimming is difficult, because the resist is too thin or bent in followed hard-mask etching. Therefore, we have developed a sequential gate process consisting ArF/polySi trimming that uses a UHF-ECR plasma. This plasma has capability to precisely CD-shift control, because of its moderate ion-current flux (ICF) at low pressure and its by-product uniformity control.[1] In polySi trimming, we evaluated the vertical undercut process. By using this process, we can measure gate-length with a CD SEM after wet etching. For vertical undercut process, we used multi-step etching, consisting a polySi main etching step with a thin side-wall protection film, followed by a highly selective trimming step. The amount of trimming could be controlled by the time of trimming step, and 86.5±1.5 nm trimming was obtained without punching through in a 2.5-nm gate-oxide layer. Regarding ArF trimming, it was confirmed that O_2 containing gas chemistry provided good hard-mask selectivity and good linearity of time control. Trimming - rate variation across the wafer was within 2.7 nm/min. To suppress resist bending in hard-mask etching, the vertical/horizontal etching rate ratio was controlled in ArF trimming, and CHF_3 based gas chemistry was used for the hard-mask etching. This good linearity of CD control with time in ArF/polySi trimming will be caused by UHF-ECR plasma that has more moderate ICF and less interaction with the reactor wall.

[1] M. Mori, et al., (2000), Proceeding of Solid State Devices and Materials, p. 192.

9:40am **PS-MoM5 Impact of Chemistry and Mask Nature on Critical Dimension Control of Gate Etch Processes**, ***X. Detter***, STMicroelectronics, France, *G. Cunge, E. Pargon, L. Vallier, O. Joubert*, CNRS/LTM, France, *R. Palla, I. Thomas-Boutherin*, STMicroelectronics, France

During a CMOS gate etch process, requirements in terms of Critical Dimension (CD) bias and microloading are more and more severe. Since gate etch processes are composed of several steps (resist trimming, BARC and probably hard mask opening, poly-silicon main etch step, soft landing step (to preserve the gate oxide) and over-etch step), a good understanding of the mechanisms influencing the CD deviation is necessary for each of them. During a classical poly-silicon gate etch process, passivation layer deposition on the gate sidewalls is known to be one source of CD microloading and the main source of CD bias for isolated patterns. However, as the aspect ratio is increasing, the profile evolution is more complicated and may be influenced by loading and shadowing effects as well as charging effects. Indeed, the passivation layer formation results from deposition of inhibitors and etching by radicals which are both strongly influenced by the nature of the mask and total aspect ratio of the structure. In this talk, we present a study of profile evolution during the poly-silicon etch steps with a resist and an oxide hard mask. Aspect ratio dependent etching and passivation layer deposition mechanisms are investigated for chemistries used in today's gate etch processes : $HBr/Cl_2/O_2$ and $HBr/Cl_2/O_2/CF_4$. Loading and shadowing effects induced by the mask are more precisely investigated (in a range of aspect ratio varying from less than 0.1 to more than 3 and a minimal space between lines of 60 nm). A correlation with X-ray Photoelectron Spectroscopy analysis of passivation layers composition and emission spectroscopy of by-products present in the gas phase is also performed. Finally, the limits of the current processes and potential strategies for future gate etch processes are discussed.

10:00am **PS-MoM6 Deposition of Silicon Oxychloride Films on Chamber Walls during Cl_2/O_2 Plasma Etching of Si**, ***S.J. Ullal***, *H. Singh, V. Vahedi*, Lam Research Corporation, *E.S. Aydil*, University of California, Santa Barbara

Chlorine plasma etching of silicon is widely used in gate etching and shallow trench isolation. During etching, the silicon chloride etch products react with oxygen present in the plasma to deposit a glassy silicon oxychloride film on the chamber walls. The chemical nature and deposition rate of the silicon oxychloride films deposited on the chamber walls during Cl_2/O_2 plasma etching of Si were investigated using multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy. The differences in the infrared spectra of films deposited under different etching conditions were quantified through the Si-O and OSi-Cl absorption band intensities and positions to determine the growth rate and composition of these films. The changes in the film's deposition rate and composition with rf bias power and O_2 flow rate gave insight into the deposition mechanism. Based on our experimental observations, we propose that the silicon oxychloride film is deposited through oxidation of $SiCl_x$ ($0 \le x \le 4$) molecules adsorbed on the reactor walls and suggest a kinetic expression for the film deposition rate. This kinetic expression may also be used judiciously for describing the silicon oxychloride deposition on the sidewalls of etched features in gate etching and shallow trench isolation.

10:20am **PS-MoM7 HBr Outgassing and Condensation from Silicon and Polysilicon Wafers after Plasma Etching**, ***H. Singh***, *D. Outka, J.D. Daugherty*, Lam Research Corporation

HBr gas is commonly used in dry etching of poly-silicon gate structures and in shallow trench etching since HBr-rich etch chemistry provides good profile control and high selectivity to gate oxide. As a result, the surface of wafers in many silicon etch processes are bromine terminated at the end of plasma etching. Subsequently, HBr outgasses from etched wafers upon exposure to atmosphere. HBr also condenses on the etched wafer and neighboring wafers in the form of HBr-hydrate and bromine-hydrate. HBr and bromine hydrates crystals are stable at ambient conditions. The timescale for HBr outgassing and condensation varies from few seconds to days, depending on the etch and ambient conditions (e.g. humidity). HBr outgassing and condensation also occurs on bare silicon wafers commonly used to condition plasma etchers before etching production wafers. The re-use of these bare silicon wafers results in micro-masking of the wafer by the HBr-hydrate crystals, resulting in formation of silicon pillars on the wafer. The micro-masking of the wafer results in formation of so-called "black silicon" rendering the wafer unusable. Various methods investigated to minimize the outgassing and condensation of HBr on wafers, including the heating of the wafer in vacuum, heating the wafer after exposure to atmosphere, and treating the wafer with oxygen plasmas, show limited success in removing bromine from the wafer surface. Separation of unetched and etched wafers on the etcher is the most effective method of eliminating micro-masking of unetched wafers. For bare silicon wafers, post treatment of the wafer with fluorine plasma is an effective way to remove the bromine from the wafer. A phenomenological model explaining the processes involved is presented, elucidating the role of chemisorbed and physisorbed bromine on the wafer.

10:40am **PS-MoM8 Energetic Neutral Fluxes Towards Surfaces in a MERIE Like Reactor**, ***W. Sabisch***, *M. Kratzer*, Infineon Technologies AG, Germany, *R.P. Brinkmann*, Ruhr University Bochum, Germany

In VLSI microelectronics fabrication Magnetically Enhanced Reactive Ion Etch (MERIE) reactors are established for many dry etch processes. One example is the etch of high aspect ratio capacitor trenches.[1] For feature scale profile evolution the angularly and energetically resolved distributions of the surfaces incident particles (ions and neutrals) as well as the fluxes of ions and neutrals play an essential role. Butterbaugh et al.[2] showed that the etch yield for the selective SiO_2 / Si etch is strongly influenced by the ratio of neutral to ion fluxes. The focus of this work is set on the calculation of the neutral to ion fluxes ratio. Therefore the MERIE reactor's boundary sheath is simulated by the TCAD simulation tool Hybrid Plasma Sheath Model (HPSM).[3,4] HPSM consists of a self-consistent coupling of a fluid dynamical part to a Monte-Carlo part. Sheath and presheath region are described in one unified model. Energetic neutrals impinging the surface can be monitored in addition to the positive ion species. Presented are simulations with parameters typical for a trench etch with pressures in the range of about 100 mTorr, rf voltages of a few 100 Vs, magnetic fields of about 100 Gauss and plasma powers of about 1000 W. The simulations show that the flux of the energetic neutrals compared to the flux of the ions is not neglectable and that the neutral flux gives an important contribution to the energy budget of the surface impinging particles.

[1] J. Bondur, R. Bucknall, F. Redeker, and J. Su: Proc. of the SPIE 1992, vol. 1803, pp. 45ff

[2] J.W. Butterbaugh, D.C. Gray, and H.H. Sawin: JVST B, vol. 34, 1991, pp. 1461ff

[3] M. Kratzer and R.P. Brinkmann: The IEEE Int. Conf. on Plasma Science 2000, 3D03

[4] M. Kratzer, R.P. Brinkmann, W. Sabisch, and H. Schmidt: JAP, vol. 90 (5), 2001, pp. 2169 ff.

11:00am **PS-MoM9 ICP Etching of Poly-crystalline Si-Ge as a Gate Material**, *K.M. Tan*, ***W.J. Yoo***, *W.K. Choi, Y.H. Wu, J.H. Chen, D. Chan*, National University of Singapore

In recently years, silicon germanium ($Si_{1-x}Ge_x$) is receiving significant attention as a candidate gate material to replace polycrystalline silicon, since Si-Ge can have advantages over poly-Si in achieving small threshold voltage and high trans-conductance required in sub 100 nm CMOS devices. In this work, we wish to demonstrate etching properties of the $Si_{1-x}Ge_x$ films using an inductively coupled plasma. The polycrystalline $Si_{1-x}Ge_x$ films were deposited by sputtering at 250°C and annealed at 900°C subsequently. The amount of Ge in the $Si_{1-x}Ge_x$ films varied from 10% to 60% by changing the sputtering target. According to preliminary results obtained using ICP of CF_4+H_2, the etching rates were strongly dependent on the amount of Ge in the $Si_{1-x}Ge_x$ films. The maximum etching rate was obtained at the chamber pressure of 20mTorr: 2.2 µ/min at 60% Ge and of 0.9 µ/min at 10% Ge when an inductive RF power of 1000W was applied. The etching rates were increased almost linearly as a function of %Ge. We were able to obtain anisotropic etching profiles over the entire experimental range of %Ge, despite that photoresist profiles prior to the ICP etching were not anisotropic. To control critical dimension of gate structures precisely and to obtain high selectivity with respect to thin oxide under-layer, we propose etching mechanisms of $Si_{1-x}Ge_x$ gates in ICP using Cl_2, HBr, and O_2, and also reveal their sidewall passivation properties.

11:20am **PS-MoM10 Endpoint Strategies for Recess Etch Processes in DRAM and eDRAM Applications**, *J.P. Merceron*, Ecole Polytechnique, France, ***V.C. Venugopal***, *A.J. Perry, A.J. Miller*, Lam Research Corporation

Developing a robust and reliable strategy to determine the end point of recess etch processes for DRAM and eDRAM applications presents some unique challenges. These processes involve etching the poly-Si back-filled into trenches in a Si substrate. The tight depth control required necessitates accounting for incoming material variations, mask erosion, and variations in the densities of incoming patterns. In addition, if an optical diagnostic tool such as an interferometer is used, the high aspect ratio structures and low open area lead to low signal levels, low fringe contrast and signal noise. Incoming nitride mask thickness could vary depending on the planarization process used (either CMP or etch) and the device being fabricated. Target depths are usually specified with respect to the bottom of the nitride layer. The starting recess depth (after planarization) is usually not known either. These uncertainties necessitate measurement of the starting nitride thickness as well as the initial recess depth to achieve the required accuracy. We have developed a robust endpoint strategy based on a broadband (UV-VIS-NIR) reflectometer, adapted to provide a high signal-to-noise ratio (SNR), to achieve the desired degree of control for recess etch processes. The broadband reflectance spectrum carries sufficient information to be able to determine the starting parameters of interest. The evolving recess structure causes a discernible modulation of the reflected light from the wafer, especially at short wavelengths (typically <300nm). A robust fringe counting method which accounts for mask erosion and etch rate variations but is insensitive to signal noise is then used to determine the change in depth of the recess relative to its initial value.

11:40am **PS-MoM11 Numerical Model of a Cl_2-BCl_3 Metal Etch Reactor**, ***G.I. Font***, *W.L. Morgan*, Kinema Research

Plasmas containing Chlorine (Cl2) and Boron trichloride (BCl3) are used in the patterning of interconnects during integrated circuit manufacturing. Optimization of the plasma uniformity in the reactor is important for the purpose of accurate pattern transfer across the entire wafer. Optimization, however, requires understanding of the influence of the reactor variables (power, pressure, and geometry) on the plasma chemistry. Simulation can aid in providing understanding of metal etch reactors by providing insight into the relative importance of chemical path ways and their dependence on reactor external variables. We have developed a chemical model for an Ar, BCL3, Cl2 discharge. Comparisons with experimental measurements inside a commercial reactor demonstrate good agreement with plasma density and electron temperature. The model also captures the plasma density distribution across the reactor and the dissociation characteristics with respect to pressure. Results below 10 mTorr suggest that parent negative ions may play an important role in the discharge.

Plasma Science
Room: C-103 - Session PS1-MoA

Dielectric Etch I

Moderator: S.H. Moon, Seoul National University, Korea

2:00pm **PS1-MoA1 Role of Fluorocarbon Radicals and Ions in SiO_2 Surface Etching Mechanism in Fluorocarbon-Based Discharges**, *X. Hua, L. Ling, X. Li,* ***G.S. Oehrlein***, University of Maryland, College Park, *M. Barela, H.M. Anderson*, University of New Mexico

To provide information on the synergistic and respective roles of FC radical and ion fluxes in SiO_2 and Si surface etching mechanisms, we measured the surface chemical changes of deposited/steady-state fluorocarbon (FC) films, etching rates of FC, SiO_2 and Si, and determined the absolute gas phase density of CF, CF_2 and COF_2 radicals as a function of RF bias and gas composition of C4F8/Ar inductively coupled discharges. Ar addition to C_4F_8 strongly increases the plasma density relative to pure C_4F_8 (~ 4x at 90% Ar), and results in a dramatic increase of the ion/neutral flux ratio for C_4F_8/90%Ar discharges relative to C_4F_8 (>20). Nevertheless, the x-ray photoelectron spectra of FC films formed on SiO_2 and Si surfaces without RF bias remain remarkably similar to those of films produced in pure C_4F_8 discharges at much lower ion/neutral ratio. Upon applying an RF bias, etching of FC, SiO_2 or Si commences. The C1s spectra of FC surface films for C_4F_8/90%Ar discharges become strongly fluorine-deficient relative to conditions without RF bias, whereas the C1s spectra of FC films formed in C_4F_8 change little. Infrared laser absorption spectroscopy was used to determine CF, CF_2 and COF_2 densities over SiO_2 and Si surfaces, with and without RF bias, and as a function of gas mixture. Without RF bias (FC deposition), the CF, CF2 and COF_2 densities do not vary with substrate type. With an RF bias, the CF_2 density over a SiO_2 surface is strongly reduced relative to a Si surface, and the change reflects the relative SiO_2/Si etch rate ratio. The composite of the results provide a fairly detailed view of the dominant surface etching mechanism and ion/neutral synergy.

2:20pm **PS1-MoA2 Characteristics of c-C_4F_8, c-C_4F_8/Ar and c-C_4F_8/O_2 Inductively Coupled Plasmas for Dielectric Etching**[1], ***A.V. Vasenkov***, University of Illinois at Urbana-Champaign, *X. Li, G.S. Oehrlein*, University of Maryland, College Park, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Fluorocarbon plasmas are widely used for etching of silicon dioxide and other dielectrics. In particular, inductively coupled plasmas sustained in c-C_4F_8 with varying amounts of diluents such as Ar and O_2 are used to produce optimum fluxes of ions and radicals. To investigate plasma chemistry in these system, reaction mechanisms were developed for inductively coupled plasmas (ICPs) and reactive ion etching reactors sustained in c-C_4F_8, c-C_4F_8/Ar and c-C_4F_8/O_2 chemistries; and implemented into a 2-dimensional plasma equipment model. The limited electron impact cross-section data for the fluorocarbon species were collected and synthesized; and rate coefficients for gas phase chemistry were taken from independent studies in the literature or estimated from measurements for related species. The final mechanisms involve 46 species and over 300 reactions. Parametric modeling studies were performed for ICPs at powers from 400 W to 1400 W and in a pressure range from 6 mTorr to 20 mTorr for c-C_4F_8, c-C_4F_8/Ar, c-C_4F_8/O_2 plasmas. The mechanisms were validated by comparing to measured ion saturation currents obtained with probes. The dominant reaction pathways and strategies to optimize desired radical fluxes will be discussed.

[1]Work supported by Semiconductor Research Corp., National Science Foundation and Sematech.

2:40pm **PS1-MoA3 Effects of Ar Gas Dilution on Precise SiO_2 Etching using CF_3I/ C_2F_4 Plasma**, *S. Samukawa,* ***H. Ohtake***, Tohoku University, Japan, *H. Ishihara, A. Koshiishi*, Tokyo Electron AT, Japan

The ϕ0.1μm high-aspect-ratio SiO_2 contact etching has successfully done using the parallel-plate commercialized etcher with the Ar-dilution C_2F_4/ CF_3I plasma. In the XPS analysis of deposition film, the radical-density ratio (for example, CF_3/ CF_2) in C_2F_4/ CF_3I does not change when Ar flow increases. However, it drastically changes in C_4F_8 gas chemistry. This could be because the C_4F_8 has complex dissociation processes. On the other hand, the radical-density ratio does not change with Ar dilution because the C_2F_4/ CF_3I gas chemistry has simple dissociation processes. Accordingly, the control of the radical densities in the C_2F_4/ CF_3I plasma could be easy by controlling the Ar flow. In this Ar/ C_2F_4/ CF_3I gas chemistry, the SiO_2 etching rate does not decrease even when Ar flow increases. However, the etching selectivity of SiO_2 to photo-resist increases when increasing the Ar dilution. Since the effect of the ion bombardment increase with Ar dilution, the C/F ratio in the deposited film on the photo-resist increases. As a result, the etching selectivity of SiO_2 to the photo-resist increases. With these conditions, the ϕ0.1μm, 10- aspect- ratio SiO_2 etching in C_2F_4/ CF_3I Ar plasma has successfully. Additionally, we investigated the leak current of MOSFET (L=0.1um, Tox: 20A) with multiple contact holes. In the threshold voltage and leak current measurement, the charging damages are not observed. Accordingly, the Ar dilution for C_2F_4/ CF_3I gas chemistry is very effective on the control of the radical densities and the increase of selectivity.

3:00pm **PS1-MoA4 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 photoresist. Profile evolution modeling can provide understanding of these difficulties in etching as well as trenching, bowing, and faceting. In this research we have measured etching and deposition rates as functions of ion bombardment energy, ion impinging angle, ion-to-neutral 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 fluorocaron plasma, 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.

3:20pm **PS1-MoA5 Electrical Conductivity of Sidewall Deposited Fluorocarbon in SiO_2 Contact Holes**, ***T. Shimmura***, *S. Soda, S. Samukawa, M. Koyanagi, K. Hane*, Tohoku University, Japan

Predicting the feature profile evolution for high aspect ratio contact hole patterning requires quantitative measurements of the sidewall conductivity in contact holes. This paper reports on On-wafer monitoring of the sidewall current in holes. We were developed the device used for measuring the sidewall conductivity. A SiO_2 film (500 nm) was deposited between Poly-Si electrodes (300 nm). The holes were fabricated by HF wet etching or conventional ICP etching. The diameter of holes was 0.5 μm, and the numbers of holes were 240000. The sidewall current was measured by supplying the voltage of 20 V between electrodes. When the holes were formed with the wet etching, the sidewall current was 4.5 nA. Conversely, it was 276.8 nA in the case of ICP etching. By removing the deposited polymer, it decreased to 40.9 nA. To clarify the influence of the deposited polymer on conductivity, we also deposited polymer in the fabricated holes using C_4F_8 UHF plasma (5mTorr, UHF power: 500W). Then, deposited polymer was exposed Ar plasma (5mTorr, UHF power: 1000W). In XPS studies, the carbon to fluorine ratio of as deposited film was 0.91. After ion irradiation, it changes to 1.86. In FT-IR spectra, characteristic absorption peaks of fluorocarbon films are appearing in 1100 - 1400 cm^{-1}.[1] The absorption that appears in neighborhood 1700 cm^{-1} was increased and shifted to low wave number by ion irradiation. This result shows that ion irradiation causes defluorination and forms unsaturated bond. Additionally, the sidewall current increased to 2181.7 nA from 38.8 nA by ion irradiation. We had found that the high cross-linked and unsaturated fluorocarbon film caused increase in sidewall current.

[1] N.M.Makie, N.F.Dalleska, D.G.Castner, and E.R.Fischer, Chem. Mater., 9 349 (1997).

3:40pm **PS1-MoA6 Silicon Oxide Highly Selective Etching Using Novel Solid Gas Sources**, ***M. Nagai***, *M. Hori, T. Goto*, Nagoya University, Japan

Dry etching of silicon oxide (SiO_2) films is an essential process for fabricating deep contact holes in ultralarge-scale integrated circuits (ULSIs). This process has been developed by using high density plasma employing perfluorinated compound (PFC) gases such as CF_4, CHF_3, C_2F_6, C_4F_8, and so on. In this process, the high selectivity of SiO_2 over resist and underlayers and the vertical etching profile for high aspect ratio patterns are required. However, there has been a problem of the poor SiO_2/resist selectivity using PFC gas source. Additionally, PFC gases of high global warming potential cause a serious environmental problem. In this study, we have developed an environmentally begin etching process without PFC gases which enables to control the radicals independently, for example CF_2

radical, C atom and F atom. In this system, the etching was performed with magnetron plasma source. The top electrode of graphite was supplied with two rf powers of 13.56 MHz and 450 kHz, which were separated through a low-pass filter. The plasma was generated by 13.56 MHz and the incident ion energy on the graphite target was controlled by 450 kHz. The bottom electrode was supplied with rf power of 2 MHz as the substrate bias. Fluorine and carbon atom sources were employed instead of PFC gases. Ar and F_2 gases as a fluorine atom source were injected into the process chamber. Carbon species were generated by magnetron sputtering of the graphite plate using Ar and F_2 gas plasma. In this etching system, the etching characteristics of SiO_2 and resist were investigated. As a result, by controlling the carbon and fluorine species incident on the surface, we have obtained the SiO_2 etching rate of 420 nm/min and high SiO_2/resist selectivity of 10 with good pattern profile of the contact holes in environmentally begin etching system without employing PFC gases.

4:00pm **PS1-MoA7 Ion-enhanced Chemical Etching of ZrO_2 in a Chlorine Discharge**, ***L. Sha****, *J.P. Chang*, University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as ZrO_2, to enable their integration in sub-0.13 µm complementary metal oxide semiconductor (CMOS) devices. In the work, we aim to study the reaction kinetics of etching ZrO_2 in chlorine chemistry in an Electron Cyclotron Resonance (ECR) high-density plasma reactor. The gas phase species, including the reactants (Cl_2, Cl_2^+, Cl, Cl^+, Cl^-, â€¦) and the etching products (zirconium chlorides and chlorine oxides), were identified with optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS). The etch rate was determined to scale linearly with the square root of ion energy in the higher ion energy regime (E_{ion} > 60 eV), indicating that it is limited by the momentum transfer to the etched film. At low ion energies, the etch rate was quite constant, likely due to reactive sputtering of the metal oxides. The etching products were found to be predominantly $ZrCl_3$ (>70%) at low ion energies. However, $ZrCl_4$ became dominant at much higher ion energies. This is likely due to the enhanced surface chlorination under higher ion energy impact. This is in good agreement with X-ray photoelectron spectroscopy (XPS) measurements, which revealed increased surface chlorine content in the film etched at higher ion energy. The concentrations of the gas phase species will be quantified with actinometry and QMS, as a function of the chlorine pressure, ion energy, and the microwave power. The etching mechanism will be proposed and the reaction rate coefficients will be calculated based on a CSTR model. CHEMKIN will be used to simulate the etching process and the results will be compared with the experimental measurement. Finally, BCl_3 will be introduced to assess its effects on the etching selectivity of ZrO_2 to Si.

4:20pm **PS1-MoA8 Ferroelectric Etching Characteristics in Ar/Cl_2 and in Ar/SF_6 Mixtures**, ***L. Stafford***, *J. Margot*, Universite de Montreal, Canada, *M. Chaker*, INRS-Energie et Materiaux, Canada

Ferroelectric materials such as barium-strontium-titanate (BST) and strontium-bismuth-tantalate (SBT) are promising for many applications, including high-k DRAMs, FeRAMs and microwave components in the millimeter wavelength range. In order to integrate these materials to various devices, the development of reliable and efficient patterning processes is a crucial issue. In this context, it was recently shown that excellent etching characteristics for BST and SBT could be achieved using a pure argon high-density plasma, provided it is operated in the very low-pressure regime (i.e. 1 mTorr or less).[1] However, scientific literature indicates that the use of reactive fluorinated or chlorinated plasmas may still improve the process. For this reason, we have investigated the etching of BST using Cl_2-Ar mixtures. The emphasis is put on the influence of the experimental conditions (total gas pressure and Cl_2 percentage in Ar) on the etch rate and on the selectivity over HPR-504 photoresist. The etching results are correlated to the plasma characteristics, including positive ion density, ion energy and reactive neutral atom concentration as obtained from various plasma diagnostics (Langmuir probes, mass spectrometry on ions and neutrals, and actinometry). Our results show that the etch rate is directly proportional to the positive ion density, whatever the experimental conditions yielding that density. This indicates that in the range of pressures investigated, the etching mechanism is dominated by sputtering. Thus, considering the fact that for given experimental conditions, the ion density in chlorine is significantly lower than in argon, the use of argon thus appears more advantageous than Cl_2 to achieve high etch rates together with a good selectivity. These results will also be compared to those obtained in Ar/SF_6.

[1] L. Stafford et al., J. Vac. Sci. Technol. A, 20(2), pp. 530-535 (2002).

***** PSTD Coburn-Winters Student Award Finalist

4:40pm **PS1-MoA9 Measuring Vacuum Ultraviolet Radiation-Induced Damage**, ***J.L. Lauer***, *J.L. Shohet, R.W.C. Hansen*, University of Wisconsin-Madison

During plasma processing, UV(ultraviolet) and VUV (ultraviolet) radiation is present, but its effects are difficult to separate from those due to charge particles incident on the wafer. To isolate the radiation effects, unpatterned oxide-coated wafers and Charm-2 wafers were exposed to UV/VUV radiation at the University of Wisconsin-Madison synchrotron. The contribution of UV/VUV photon irradiation to gate-oxide damage, and damage to dielectric materials in general, were examined using two measurement techniques that may predict the possibility of damage. They are (1) surface potential measurements and (2) electrically erasable read-only memory transistors (Charm-2 Wafers). In addition to these measurements, the current flowing to the wafer and the voltage on the substrate, were monitored during photon irradiation. Two processes, photoemission and photoconductivity, can create currents flowing across the dielectric layer, while only photoemission occurs in conductors. Positive charge appearance on the surface of dielectrics and conductors by VUV photoemission results in extraneous charge measurements with both techniques. As a result, it can become difficult to interpret the net amount charge on surfaces. In addition, it was determined that the UV monitors on Charm-2 wafers do not respond to VUV radiation.[1] Thus, the results from both damage measurement techniques must be analyzed carefully, especially in situations where VUV generation is important, such as in processing plasmas.

[1]The authors are grateful to W. A. Lukaszek of Wafer Charging Monitors and John Hu of LSI for loaning us the Charm-2 wafers and providing the analysis of the UV/VUV exposures. This work was supported in part by the National Science Foundation under grant DMR-0084402

5:00pm **PS1-MoA10 Transfer of Resist Roughness into Substrates during Plasma Etching**, ***A.P. Mahorowala***, *D.L. Goldfarb, G.M. Gallatin, D. Pfeiffer, K.E. Petrillo, K. Babich, M. Angelopoulos*, IBM T.J. Watson Research Center

Traditionally photoresists have been evaluated on the basis of their lithographic process latitude and etch resistance. For sub-150 nm process technologies, this is inadequate because the deviations in linewidth caused by a photoresist's inherent roughness and transferred into the substrate during etch can be comparable to the maximum allowable tolerance. The photoresist roughness issue has been exacerbated by the introduction of 193 nm photoresists whose films are not only thin but whose etch resistance is poorer than the 248 nm photoresists widely used. The photoresists used in conjunction with 157 nm and EUV lithographies are expected to be even thinner. This paper systematically studies the roughness transfer into an oxide substrate when using 248 nm, 193 nm and 157 nm photoresists in conjunction with organic and inorganic anti-reflective coatings/hard masks. Photoresist thickness, minimum feature size, plasma etch chemistry and time were varied as a part of this study. The analysis is based on cross-sectional and top down SEM micrographs and careful measurement of the sidewall roughness using AFM. The relative contributions of the photoresist material, development conditions, and the etching conditions to the roughness of the final image are determined and explained. Recommendations to prevent roughness transfer into the substrate are made.

Plasma Science
Room: C-105 - Session PS2-MoA

Plasma Processing for Large Area Substrates
Moderator: D. Leonhardt, US Naval Research Laboratory

2:00pm **PS2-MoA1 Ion Flux Uniformity in Large Area High Frequency Capacitive Discharges**, ***A. Perret****, *P. Chabert, J. Jolly, J.P. Booth, J. Guillon*, Ecole Polytechnique, France

Etching and thin film deposition using capacitive RF discharges at 13.56 MHz are routinely used for Flat Panel Display fabrication. The current trend in FPD technology is to increase the substrate size (> 1m2) while keeping high throughput (> 50 glass/hour). Very High Frequency (VHF) plasma excitation promises to provide faster processes whilst avoiding damage due to high energy ion bombardment. However, the reactor size may no longer be negligible with respect to the wavelength of the RF electromagnetic wave, causing non-uniformity in the plasma density across the reactor. The physical origin of this phenomenon is the beginning of a spatial standing wave within the reactor. The standing wave effect will become more important as the frequency is increased. Other phenomena causing non-uniformity will appear if the skin depth become small compared to the reactor size. We will present an experimental study of the ion flux uniformity of a plasma created in a large area capacitive discharge driven at frequencies of 13.56 to 60 MHz. The discharge was produced between two

square plates (40cm x 40cm) separated by a distance of 8 cm. The ion flux variation across the reactor is measured by a system composed of 64 electrostatic probes inserted in the grounded upper electrode and biased negatively. The probes are regularly spaced and the time to read all probes is less than 2 seconds. The experimental results will be compared with a recently proposed model (Lieberman et al. Plasma Sources Science and Technology, accepted 2002).

2:20pm **PS2-MoA2 Electrical Characterization of Linearly Extended Inductively Coupled Plasma Sources for Large Area Processing**, ***Y.J. Lee***, *K.N. Kim*, Sunkyunkwan University, South Korea, *S.E. Park, J.K. Lee*, Pohang University of Sci. and Tech., South Korea, *G.Y. Yeom*, Sunkyunkwan University, South Korea

In order to achieve the performance required for high resolution flat panel display (FPD) devices, especially for TFT-LCD of next generation, improved dry etch processes currently indispensable technology for semiconductor industry are required for volume manufacturing and superior critical dimension control. The plasma sources developed to date for the production of high-density and large-area plasmas mainly focused on the spiral-type planar external ICP sources. However, due to its large inductance with the scale-up to larger areas and the cost and the thickness of its dielectric material, the conventional ICP source using an external spiral antenna may have reached its limit in extending the process area. Therefore, in this study, a plasma source utilizing inductive coupling of linear extended internal antennas has been used as a candidate for the efficient large area high-density plasma source. To minimize the inherent electrostatic coupling effect in the internal inductive linear antenna configurations, various internal-type linear antenna designs have been used in a square shaped (830mm*1,020mm) plasma chamber. Characterization of the system impedance for the various internal-type antenna schemes were achieved by measuring the current, the voltage, and the phase angle difference at 13.56MHz using a V/I probe (ENI). It was found that there was a significant change in inductance depending on the type of linear antenna designs. A simple modeling and simulation with a 2-D fluid code were also used to analyze the optimum arrangement and the distance of the each line source. In this presentation, the effects of various arrangements of the linear antennas and process conditions on the plasma characteristics were investigated using a quadrupole masss spectrometer (QMS: Hidern Analytical Inc., PSM 500) and a Langmuir probe (Hiden Analytical Inc., ESP) located on the sidewall of the chamber and the results were compared with the simulation data.

2:40pm **PS2-MoA3 Optimization of Source Modules in ICP-Helicon Multi-Element Arrays for Large Area Plasma Processing**, ***J.D. Evans***, *F.F. Chen*, University of California, Los Angeles

Optimization studies of compact inductive rf-source modules for use as individual elements of a multi-element ICP-helicon source array, with sufficient density N and spatial N(R) profile uniformity for plasma processing of arbitrarily large substrates, is described. Attention is restricted to a low-magnetic-field (low-B) regime (B < 250G), within which a local maximum (low-B peak) in N vs B is routinely observed and exploited for optimum plasma production efficiency. Proof of principle experiments that exploit this low-B peak have been successfully performed [PSST 10, 236 (2001)] in Ar and Cl. Arrays consisted of 7 cylindrical Pyrex tubes (o.d. = 5cm) plus antennas, with center-to-center spacing = 2d, mounted in a honeycomb pattern on top of a magnetic bucket. Optimization of individual modules of various aspect ratios and sizes are the focus of the present work. Static Bo is provided by a combination of coils and ring-shaped permanent magnets in close proximity to each module, designed such that they can fit in a usable multi-element source of arbitrarily large area. Measurements of N(R) vs B, at RF powers Prf < 1.6kW and neutral pressures Po = 1-25 mTorr, as well as radial N(R) profiles obtained from Langmuir probes vs axial distance are obtained. Anomalous enhancement of N(R) uniformity is observed when the low-field peak condition is met, with "flat" density profiles extending 5 tube radii, at axial distances < 2 tube diameters below the mouth. The implications for large area plasma processing applications are discussed.

3:00pm **PS2-MoA4 Scaling up of a Magnetic Pole Enhanced Inductively Coupled Plasma Source (MAPE-ICP)**, *P. Colpo*, ***T. Meziani***, *F. Rossi*, European Commission, Joint Research Centre, Italy

The principles of a Magnetic Pole Enhanced Inductively Coupled Plasma are presented. Plasma characterisation made on a 200mm source show that the electrical coupling efficiency is increased by a factor 4 as compared to a conventional flat coil configuration. Scaling up of the reactor to the dimension of 800x800mm poses several technological problems that have been solved and are presented. Characterisation of the large scale source show that a plasma density of 2 to 4 E11cm-3 with an Ar plasma at 2MHz is obtained and an homogeneity of the ion current density better than 20% over 800mm. Application of the source to the etching of SiO2 layers is presented. Etching rates of the order of 100nm/mn are obtained over the whole area. Results of plasma characterisation and chemistry are presented.

3:20pm **PS2-MoA5 Plasma Processing for Large Area Substrates**, ***V. Cassagne***, *M. Elyaakoubi*, UNAXIS France **INVITED**

In the liquid crystal flat panel display industry, the large area has another meaning than in semiconductor business. First, in size , the starting generation in the early 90's was in the range of 300x400mm glass substrate, now (5^{th} generation) the average size is 1100x1250 mm (higher productivity, higher flexibility). Second is the generation cycles : in 12 years, the market generated 6 size generations without real sizes standards. Now with more than $1.4m^2$ substrates, in parallel of economic and production pressure, we have to face Physics challenges in addition to standard engineering issues. Both for PECVD, PVD and dry etching processes, we have to deal with new phenomenon linked to the dimensions. There are first mechanical (loading 0.5mm thick substrate, thermal expansion, atmospheric pressure stress), then thermal (temperature process uniformity, heating/cooling power and time), gas flow (as diffusion length is smaller than reactor size local defaults are exhibited), RF electric field uniformity (now electrode dimensions start to be not negligible compare to RF wavelength, local field disturbances affect the process uniformity due to diffusion limitation). In addition, production trends require higher throughput (higher deposition rate, faster plasma cleaning), higher yield (low particles, lower defaults), higher up-time (higher reliability, easier maintenance), smaller footprint (compact solution, parallelism). It leads to R&D programs like plasma uniformity (gas flow, RF field, plasma chemistry), arcing-free plasma, up-scalable concepts and target utilization optimization for PVD and PECVD and high density source for Dry Etching. All these topics are evaluated by numerical modeling and experimental set-up. Advanced materials, laboratory tests and prototyping are used in order to prepare new plasma system generations.

4:00pm **PS2-MoA7 High-rate Large-area Plasma Deposition using Multiple Expanding Thermal Plasmas**, ***M. Schaepkens***, *C.D. Iacovangelo*, General Electric Global Research Center

A unique, high rate, large area plasma deposition process has been developed to generate various functional coatings on polymeric substrates. The process relies on the integration of a plurality of individual expanding thermal plasma sources into a multi-source setup. In this work we will discuss the effects of various hardware (e.g. reagent injection configuration) and process (e.g. pressure, reagent flow, preheat) parameters on the performance of a dual-source system that has been used to apply abrasion resistant coatings to polycarbonate substrates. It will be shown that a properly engineered dual-source system can generate transparent, organosilicon-based coatings that provide uniform, glass-like abrasion resistance across substrates up to 30 cm x 30 cm. Multi-source systems comprising more than two plasma sources hold promise for generating even larger area uniform coatings.

4:20pm **PS2-MoA8 Reflective Enhancement of Distributed Helicon Sources**, ***F.F. Chen***, University of California, Los Angeles

In Ref. 1 it was shown that large-area substrates can be covered uniformly with dense plasma by using a plurality of short helicon sources.[1] In this source use was made of the "low-field peak" (LFP), a density peak occurring near B = 50G which had been observed in several helicon devices.[2] A very quiet, stable discharge could be obtained in the neighborhood of this peak.[3] This feature was not predicted by standard helicon theory and was unexplained. In the latest version of the code HELIC developed by Arnush,[4] it is possible to model a short helicon source bounded at one end. The LFP is produced by constructive interference by the reflected wave from an end plate near the antenna and not, for instance, by a resonance of the Trivelpiece-Gould mode. This mechanism can also explain previous observations[5] of density enhancement by flaring magnetic fields or inserted blocks. This knowledge permits design of more compact helicon reactors.

[1]F.F. Chen, J.D. Evans, and G.R. Tynan, Plasma Sources Sci. Technol. 10, 236 (2001).
[2] F.F. Chen, X. Jiang, J.D. Evans, G. Tynan, and D. Arnush, Plasma Phys. Control. Fusion 39, A411 (1997).
[3]F.F. Chen, J. Vac. Sci. Technol. A 10, 1389 (1992).
[4]D. Arnush, Phys. Plasmas 7, 3042 (2000).
[5]G. Chevalier and F.F. Chen, J. Vac. Sci. Technol. A 11, 1165 (1993).

Plasma Science
Room: C-105 - Session PS+MS-TuM

Plasma Diagnostics and Sensors
Moderator: R.J. Shul, Sandia National Laboratories

8:40am **PS+MS-TuM2 High-energy EEDF Tail Detection in High-frequency Discharges**, ***J. Kudela***, *K Suzuki, Y. Nakagawa, Y. Numasawa,* ANELVA Corporation, Japan, *T. Beppu,* RITE, Japan

It is well-known that the enhanced high-frequency (HF) fields in the oscillating plasma sheaths can lead to generation of high-energy electrons. At sufficiently low gas pressures, this phenomenon is crucial for the discharge maintenance. However, the phenomenon may also cause the discharge instabilities. The detection of the high-energy tail in the electron energy distribution function (EEDF) in HF discharges is, therefore, of a particular interest from the scientific point of view. It is also important from the technological point of view. The high-energy electrons are determining factor in processing plasmas affecting the discharge chemistry in the plasma volume, and on the processing surface as well. Moreover, on the processing surface, the high-energy electrons may also be responsible for undesired physical processes like charge damage. In our work, we illustrate the detection of high-energy electrons by electrostatic probes in HF discharges at two different frequencies, 2.45GHz and 60MHz. In the microwave band (2.45GHz), the detection of the high-energy electrons is rather simple and it requires only direction-sensitive probes.[1] Similar technique is applied to the VHF band (60 MHz) discharges. In these discharges, however, a proper probe compensation is necessary. The conventional compensation methods, which are based on sensing floating potential fluctuations around the probe tip, lose information about the EEDF tail. We propose a method that can lead to detection of high-energy electrons, as well as to the diagnostics of the VHF discharges. This work is supported by NEDO.

[1] J. Kudela, T. Terebessy, and M. Kando: Hot electrons and EEDF-anisotropy in large-area surface-wave discharges; Proc. IV Int. Workshop Microwave Discharges: Fundamentals and Applications, Sept. 18-22, 2000, Zvenigorod, Russia; ed. Yu.A. Lebedev (Yanus-K, Moscow, 2001), p.63.

9:00am **PS+MS-TuM3 Coupled Diagnostic Studies of Plasma Etch Byproducts**, ***M.T. Radtke***, *D.B. Graves, J.W. Coburn*, University of California Berkeley

Plasmas used for etching invariably include species that originate at surfaces. Etch byproducts commonly play a major role in plasma composition, in addition to influencing etch rate, anisotropy, critical dimension control, and selectivity. Etch byproducts often deposit on chamber walls, altering wall chemistry such as radical recombination reactions, and leading to the formation of particles. Chamber wall cleaning and conditioning protocols can play an important role in etch tool cost-of-ownership. For new high-k and low-k dielectrics and metal gate electrode materials, the etch characteristics and etch byproducts are usually not known. In addition to posing a challenge for feature critical dimension control and other etch objectives, the unknown etch byproducts may pose environmental, health and safety hazards. We reports studies using an inductively coupled plasma reactor equipped with a cooled, rf-biased chuck, a downstream FTIR spectrometer, a quartz crystal microbalance, a Langmuir probe, an ion flux wall probe, an ion mass spectrometer, a separate threshold ionization mass spectrometer for neutral radical detection, and optical emission spectroscopy. We have employed this system to measure etch byproducts and etch byproduct transport for a range of new high-k and low-k dielectric materials as well as candidates for metal gate electrodes. We illustrate the use of coupled plasma diagnostics for ZrO_2/Cl_2, SiO_2/CF_4, RuO_2/O_2, HfO_2/Cl_2, and $Si/Cl_2/O_2$. In particular, detection and identification of low volatility byproducts can be challenging, and often require combining information from the ion mass spectrometer, the neutral mass spectrometer, film composition measurements on the quartz microbalance, optical emission spectroscopy, and the downstream gas composition.

9:20am **PS+MS-TuM4 Two-Dimensional Ion Flux Distributions on the Wafer Surface in Inductively Coupled Plasma Reactors**, ***E.S. Aydil***, *T.W. Kim,* University of California, Santa Barbara

A two-dimensional array of planar Langmuir probes manufactured on a 200 mm diameter silicon wafer was used to measure the radial and azimuthal variation of ion flux impinging on the wafer surface in various mixtures of electropositive and electronegative gases maintained in an inductively coupled plasma etching reactor. The spatial variation of ion flux in a pure Ar discharge is radially symmetric and peaks at the center of the wafer for pressures between 10 and 60 mTorr. Addition of small amounts of electronegative gases to an Ar discharge flattens the radial and azimuthal ion flux distribution and accentuates azimuthal variation due to subtle asymmetries in the reactor geometry such as pumping ports. At fixed power, pressure, and flow rate, the spatially averaged ion current density decreases with increasing mole fraction of the electronegative gases in the feed gas. In conjunction with experimental data, we developed a simple theoretical framework within which the spatial variation of ion flux in gas mixtures can be understood. Ion Flux uniformity in various binary mixtures of Cl2, He, Ar, HBr, O2, and SF6 will be discussed. Spatiotemporal variation of ion flux in presence of instabilities in SF6 discharges will be presented.

9:40am **PS+MS-TuM5 Surface Dependent Effects at the Plasma-Surface Interface**, ***G.A. Hebner***, Sandia National Laboratories **INVITED**

In a typical etching application, a number of different materials from the common silicon, and silicon oxide to more exotic nitrides and low-k materials can be located in very close proximity to each other. The interaction of these different materials through changes in the plasma chemistry, non-equilibrium surface layers and local electric field is of fundamental interest since the local chemistry and plasma properties determine the characteristics of the resulting etch profile. A number of techniques have been used to characterize etching plasmas as a function of the surface material. Plasma species such as CFx, SIFx and BCl radials have been measured as functions of the surface material and radial position using laser induced fluorescence. Those measurements show significant changes in radical species concentration for silicon, silicon oxide and ceramic surfaces. Measurements of the electron and negative ion density using a microwave interferometer and laser photodetachment also show surface dependent changes in the bulk plasma chemistry. In addition to the plasma chemistry, the sheath electric field is of interest since it's magnitude and vector guide the ion species. Of particular interest is the measurement of the material dependent surface charging, a task that is challenging considering the required spatial, temporal and electric field sensitivity. An atomic beam system combined with pulsed laser spectroscopy has been used to directly calibrate the electric field induced Stark shift of high lying energy levels. Measurements of the electric field within an inductively driven argon discharge will be discussed. The possibility of using this system to calibrate energy level shifts in other gases of technological interest to the microelectronics and lighting industry will be discussed. This work was supported by the United States Department of Energy (DE-AC04-94AL85000).

10:20am **PS+MS-TuM7 Monitoring Sheath Voltages and Ion Energies in High-Density Plasmas using Radio-Frequency Current and Voltage Measurements**, ***M.A. Sobolewski***, National Institute of Standards and Technology

The bombardment of substrate surfaces by energetic ions plays an important role in plasma etching and other plasma processing applications. To obtain optimal results, ion kinetic energies must be carefully controlled. However, measuring ion energy distributions in situ, at a wafer surface during plasma processing, is difficult or impossible. A method for indirectly monitoring ion bombardment energies would thus be useful, both as a source of information to guide process development and as a tool for process monitoring and control in manufacturing. Accurate ion energy distributions can be calculated by models of plasma sheaths if one knows the sheath voltage, the electron temperature, and the total ion flux. These parameters are in turn related to radio-frequency (rf) current and voltage signals that can be measured outside a plasma reactor, without perturbing the plasma or the process. Indeed, several different model-based methods have been proposed for using rf current and voltage measurements to determine sheath voltages and ion energies. In this study, three such methods were tested. Tests were performed in argon and CF_4 discharges at 10 mTorr, in an inductively coupled, high-density plasma reactor. All the methods were able to successfully detect changes in sheath voltages and total ion flux, and to infer the effect of these changes on ion energy distributions. However, the rf measurements are relatively insensitive to changes in the electron temperature. To obtain the most accurate sheath voltages and ion energies from rf measurements, the electron temperature should be known ahead of time, or monitored by some independent measurement technique.

10:40am **PS+MS-TuM8 Gas Temperature Effects on CF_x Kinetics in a CF_4 Inductively Coupled Plasma**, *H. Abada,* ***J.P. Booth***, *P. Chabert,* Ecole Polytechnique, France

We have used Laser Induced Fluorescence to determine CF and CF_2 radical concentrations in steady state and pulse-modulated inductively-coupled plasmas in CF_4 at 5 and 33 mTorr. The rotationally-resolved LIF excitation

spectra of the CF radical were used to determine the space and time resolved gas temperature. Strong temperature gradients were observed, with the temperature reaching 800 K in the reactor center at 33 mTorr, 250 W RF power. These measurements were used to correct the LIF measurements for the dependence of the partition function on the gas temperature, providing the first reliable measurements of CF and CF_2 kinetics in this system. The concentration profiles can be used to deduce the net flux of these species from or to the reactor walls, using Fick's law but also allowing for thermo-diffusion. The steady-state CF_2 profiles showed that this species is produced predominantly at the reactor walls by CF_x^+ ion bombardment. Surprisingly, in the post-discharge the CF_2 density increases markedly for several milliseconds, before decaying slowly. We will explore the possible origins of this phenomenon, which include convection induced by gas cooling, vibrational relaxation and conversion of CF to CF_2 by chemical reaction. In contrast, the CF radical appears to be both produced and destroyed in the gas phase, and it's concentration decays monotonically and rapidly in the post-discharge.

11:00am **PS+MS-TuM9 Electron Energy Distribution in C_2F_4/CF_3I Ultrahigh-Frequency and Inductively Coupled Plasmas**, ***T. Nakano***, National Defense Academy, Japan, *S. Samukawa*, Tohoku University, Japan **INVITED**

The electron energy distribution function (eedf) is an important factor in determining radical compositions in plasmas for nanometer-scale device fabrication. In this presentation, the electron energy distribution in plasma through a C_2F_4/CF_3I mixture, which is a novel chemistry proposed for low-damaged, fine structure etching of SiO_2, is studied by trace rare gas optical emission spectroscopy (TRG-OES) and probe measurements. The integrated eedf above 13.5 eV (S_{eedf}) is evaluated from the Ar emission at 750.4 nm. The S_{eedf} exhibits a weaker dependence on the gas composition for the C_2F_4/CF_3I mixture than for the C_4F_8/Ar mixture which is conventional chemistry for SiO_2 etching. For practical etching conditions, the S_{eedf} for the C_2F_4/CF_3I mixture becomes smaller than 1/3 of that for the C_4F_8/Ar mixture in both ultrahigh-frequency (UHF) plasmas and inductively coupled plasmas (ICP). Thus, using the C_2F_4/CF_3I chemistry, low charging damage in SiO_2 etching is expected. The probe-measured electron temperature (T_e), which indicates the degree of the exponential eedf decay in the low energy, is 2.5 eV in UHF plasma through the C_2F_4/CF_3I mixture and 4.1 eV in the ICP, while S_{eedf} is twice as large in the UHF plasma as in the ICP. This suggests an eedf enhancement in the middle energy region (5-10 eV) for the ICP, which prompts the dissociation of the feedstock gases. A quantitative estimation of the eedf using a bi-Maxwellian-like function, which is crucial to understanding the relationship between the eedf and feedstock gas dissociation, is in progress. The preliminary results also support the eedf enhancement in the middle energy region for the ICP.

11:40am **PS+MS-TuM11 Dependence of Radical Densities on Fluorocarbon Feed Gases in a Dielectric Etch Plasma**, ***E.A. Hudson***, *J. Luque*, Lam Research Corp., *N. Bulcourt, J.P. Booth*, Ecole Polytechnique, France

Unsaturated fluorocarbon gases are increasingly important for critical dielectric etch applications. Under typical plasma etch conditions, these feed gases promote the deposition of fluorocarbon polymer films. Using process parameters to tune the polymer deposition characteristics, one can control the critical dimension and profile of the etched feature, and minimize the loss of the photoresist mask. Different unsaturated fluorocarbon gases produce different process results, for reasons which are poorly understood. In an effort to better understand these differences, the plasma radical composition has been analyzed for a range of feed gases including the unsaturated fluorocarbons octofluorocyclobutane(C_4F_8) and octafluorocyclopentene (C_5F_8), and also a saturated compound, perfluoroethane (C_2F_6). Optical emission spectroscopy (OES) and broad-band UV absorption spectroscopy (UVAS) have been used to measure radical densities in a dual-frequency, capacitively-coupled, dielectric etch reactor. Species detected include CF, CF_2, and F. Notable variations in radical densities were observed for a series of processes based on Ar, O_2, and one of the fluorocarbon feed gases. CF_2 density, in particular, showed a strong dependence on fluorocarbon feed gas. The F/CF2 density ratio increased by more than a factor of 2 when C_2F_6 was substituted for C_5F_8. For each fluorocarbon feed gas, the sensitivity to changes in the O_2 flow has been evaluated. Results suggest that the role of oxygen in controlling polymer film thickness in and around etched features is related to polymer formation as well as polymer removal.

Plasma Science
Room: C-103 - Session PS-TuM

Atmospheric Pressure and Other Emerging Plasma Applications
Moderator: R. Blumenthal, Auburn University

8:20am **PS-TuM1 Instabilities in a Dielectric Barrier Discharge at Atmospheric Pressure**, *M.C.M. Van de Sanden*, ***E. Aldea***, Eindhoven University of Technology, The Netherlands, *C.P.G. Schrauwen*, TNO TPD, The Netherlands

Due to their enormous potential for cost-efficient industrial applications, atmospheric low temperature (300-500 K) plasmas at atmospheric pressure received large attention in recent years. From the points of view of power density and plasma stability the most efficient solution was proved to be the dielectric barrier configuration in which the electrodes are covered with a insulator. The procedure used to generate plasma is simple but the physical mechanism underlying the plasma generation is still unclear. The generation of homogeneous plasma at atmospheric pressure is assumed to be related to the gas pre-breakdown pre-ionisation by metastable-metastable collisions,[1] but there are not yet unambiguous experimental evidences of a significant pre-ionization due to this mechanism. In this paper the work was focussed on the investigation of the role of metastables in the excitation or ionisation processes in a plasma generated in Ar , nitrogen and air between two electrodes (electrode gap 0.3-5 mm) covered by a dielectric mounted in a gas tight cabinet. A study of dependence of plasma stability and filamentation on the electrode gap, surface temperature, voltage pulse frequency or shape was also performed and the optimum conditions range was defined. The importance of metastables is evaluated on basis of the plasma rovibrational and excitation temperatures derived from the optical emission spectroscopic data, and on the study of the correlation between temporal dependence of the plasma emission and of the current pulse. It is demonstrated that metastable-metastable collisions cannot be responsible for a significant pre-ionization. Therefore other factors must play a role in plasma stability.

[1]N. Gherardi, G. Gouda, E. Gat, A. Ricard, F. Massines , Plasma Sources Sci. Technol. 9 (2000), 340.

8:40am **PS-TuM2 Atmospheric Pressure Plasma Processing**, ***R.F. Hicks***, *G.R. Nowling, M. Moravej, X. Yang*, University of California, Los Angeles, *G. Ding*, Applied Materials, *S.E. Babayan*, Surfx Technologies LLC **INVITED**

Atmospheric pressure plasma discharges have emerged as exciting new tools for materials processing. There are many different sources to choose from depending on the application, including dielectric barrier discharges, microwave plasmas, transferred arcs and inert-gas-stabilized capacitive discharges. At UCLA, we have developed a novel low-temperature plasma source, in which reagent gases are mixed with helium or argon and passed through two closely spaced, perforated electrodes. By applying radio frequency power at 13.56 to 100.0 MHz to one of the electrodes, the gas becomes ionized with the dissociation of about 1% of the reagent molecules into atoms and radicals. This source exhibits a charged particle density of about 10^11 cm^-3 and an electron temperature from 2 to 4 eV. By contrast, the neutral temperature ranges from 300 to 450 K, depending on the process conditions. Many different gas mixtures may be fed through the source, including oxygen, nitrogen, hydrogen, carbon tetrafluoride, ammonia, etc. The concentration of ground-state atoms, e.g., O or N, varies from about 1.0 to 10.0 x10^15 cm^-3. These species may be used to drive a variety of downstream surface treatment processes, including polymer activation, organic residue removal, glass or metal etching, and chemical vapor deposition. At the meeting, I will briefly review atmospheric pressure plasma sources, and then describe our work on the physics and chemistry of these systems.

9:20am **PS-TuM4 Atmospheric Pressure Plasma Treatment of Polypropylene**[1], ***R. Dorai***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Atmospheric pressure plasmas, corona and dielectric discharges in particular, are used to modify polymer films to improve their wetting and adhesion properties. Production of O and OH radicals in humid air discharges produce surface oxidation of the polymer and result in the formation of Low-Molecular Weight Oxidized Material (LMWOM). Although a widely used industrial process, the fundamental plasma surface interactions which produce LMWOM and modify surface properties are not well understood. In this paper, results from a computational investigation of corona treatment of polypropylene will be discussed with the goal of determining the reaction mechanism which produce LMWOM. The investigation was performed using a global plasma chemistry model linked

with a surface site balance model for the plasma-surface interactions. The surface reaction mechanism distinguishes between processes which produce hydrophilic and hydrophobic groups. Comparisons can then be made with experimental data for corona treated polypropylene based on wettability (contact angle), densities of different surface groups and erosion rates. With the validated reaction mechanism, parameterizations of the important variables affecting the adhesion properties namely, energy deposition and relative humidity will be performed.

[1]Work supported by 3M, Inc. and the National Science Foundation.

9:40am **PS-TuM5 Simulation of the Plasma Dynamics and Chemical Phenomena in Dielectric-barrier Controlled Atmospheric-pressure Glow Discharges**, ***X. Yuan***, *L. Raja*, University of Texas at Austin

Large-volume atmospheric-pressure glow (APG) discharges 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 plasma parameter space and have properties that resemble classical low-pressure glow discharges, but at atmospheric or near-atmospheric pressures. Important classes of APG discharges include a high-frequency capacitively coupled configuration with closely spaced parallel electrodes and a low-frequency dielectric-barrier configuration with parallel plates and an intermediate dielectric layer. In this talk, we will present detailed one-dimensional simulation results for a dielectric-barrier APG discharge for varying discharge parameters such as gap length, dielectric capacitance, and frequency. The mechanism of pulsed glow formation and extinction will be discussed for a noble gas (helium) and a molecular gas (nitrogen) APG plasma. Ion impact energy characteristics at the surfaces will be analyzed and its implications for in situ material processing will be reported. Simulation results will be verified with experimental data where available.

Supported by NSF-CAREER grant.

10:00am **PS-TuM6 Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon at Atmospheric Pressure**, ***M. Moravej***, *S. Babayan, G.R. Nowling, X. Yang, R.F. Hicks*, University of California, Los Angeles

The plasma enhanced chemical vapor deposition (PECVD) of hydrogenated amorphous (a-Si:H) and hydrogenated microcrystalline (uc-Si:H) silicon has been examined at ambient pressure. A hydrogen and helium gas mixture flowed through two electrodes supplied with 50 W RF power at 13.56 MHz. Silane was added downstream from this plasma, and the reactive mixture directed onto a heated glass substrate. After growth the thickness of the films was determined using a profilometer. The deposition rate increased with the H2 and SiH4 partial pressures and saturates at approximately 70 Å/min for both parameters. The deposition rate also increased with substrate temperature following an Arrhenius relation with an activation energy of 3.44 kJ/mol. However the growth rate decreased from 92 Å/min to 13 Å/min as the electrode-to-substrate distance increased from 10.5 mm to 5 mm. Fourier-transform infrared spectroscopy, Rutherford backscattering spectroscopy, and Raman spectroscopy were used to determine the structure and chemical composition of the films. The effect of the process conditions on the hydrogen content and degree of crystallinity of the films will be discussed at the meeting.

10:20am **PS-TuM7 Low Energy Electron Enhanced Etching (LE4) for Reduced Process Damage in Compound Semiconductor Devices**, ***H.P. Gillis***, *S.H. Lee*, University of California, Los Angeles, *D.I. Margolese, S.J. Anz*, Systine, Inc. **INVITED**

Dry etching for defining device features is a key process in manufacturing integrated circuits because it controls critical dimensions much more tightly than does wet etching. Indeed, the ability to etch transistor features at dimensions progressively smaller than 0.25 ?m has been a mainstay of the computer industry, and is one of the foundations of Moore's Law. As a side effect, the conventional dry etch methods inflict "etch process damage" caused by the surface ion bombardment needed for high resolution feature definition. Consequently, the need arises for developing alternative dry etch processes and for characterizing "etch process damage" in material terms to guide its control and elimination. We will describe an alternative dry etch method in which electrons with energies below about 15 eV stimulate high-resolution etching of features as small as 0.020 ?m with no apparent damage. Along with high-resolution feature definition, this method gives mirror-smooth etched surfaces and maintains stoichiometry of compound materials. We will relate these results to plasma conditions including the electron temperature and energy distribution. The discussion will emphasize compound semiconductor materials and applications for optical and wireless communications.

11:00am **PS-TuM9 Coulomb Crystals in Plasma Processing Reactors**[1], ***V. Vyas***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

Many plasma deposition systems operate in regimes whereby large densities of small particles are nucleated in the gas phase. Given sufficient densities of these particles, they can exhibit collective behavior and form Coulomb solids. These structures typically form at moderate gas pressures, small particle sizes and lower powers in capacitively coupled, radio frequency discharges. Lattices having different radial structure functions [g(r)], non-ideality factors and geometrical shapes can be formed given somewhat subtle changes in discharge properties. Having scaling laws for their behavior would be desirable to minimize unwanted feedback to the plasma or film properites. To address these phenomena, a 3-dimensional dust transport simulation has been developed and incorporated into a plasma equipment model. The forces included in the dust transport model are electrostatic, ion-drag, thermophoretic, fluid-drag by neutrals, gravity and particle-particle Coulomb interactions. We will discuss formation of plasma crystals as function of operating conditions in rf discharges and, in particular, the formation of voids in the plasma crystal at high substrate biases. The negative ion fluxes in electronegative gas mixtures alter the ion drag force acting on the dust particle leading to qualitatively different crystal morphologies than those found in electropositive plasmas. For example, addition of electronegative gases such as Cl_2 and O_2 to Ar causes voids in the plasma crystals to close. The effect of ion streaming on dust particle motion will be discussed, as will the effect of surface topology on radial compression of the plasma crystal producing changes in interparticle spacing and g(r).

[1] Work was supported by Sandia National Laboratory and the National Science Foundation.

11:20am **PS-TuM10 Simplified Model for Calculating the Pressure Dependence of a DC Planar Magnetron Discharge and Experimental Verification**, ***G. Buyle****, *D. Depla, K. Eufinger*, Ghent University, Belgium, *W. De Bosscher*, Bekaert Advanced Coatings, Belgium, *J. Haemers, R. De Gryse*, Ghent University, Belgium

A simplified model for the DC planar sputter magnetron discharge allowing to simulate the pressure dependence over a wide range is presented. The model is based on the assumption that the discharge is built up by arch shaped regions which are determined by the orbits of the electrons emitted from the cathode by ion bombardment (secondary electrons). This assumption, combined with relatively simple schemes for the ionization, target erosion and secondary electron production, forms the core of the simplified model. Although the presented model has not the same accuracy as more advanced models based on the Monte-Carlo method, it has the major advantage of being much less computing intensive. This allows for quickly assessing the influence of a variety of discharge parameters and has proven to be well sufficient to explain our experimental results. We observed that at high gas pressures (above approximately 0.5Pa) there is a very weak pressure dependence of the observed discharge parameters, but for lower pressures an increase in the discharge voltage, cathode sheath thickness and erosion profile width is observed. Our modeling revealed the necessity to integrate recapture of secondary electrons by the cathode to explain the observed pressure dependence. To our knowledge, recapture in planar magnetron discharges has not been acknowledged yet. This is because the small initial energy of the secondary electrons, which enables recapture, is neglected in recently published simulations. Given the good agreement between experiment and simulation in this study, it appears that recapture is essential for accurately modeling the planar magnetron discharge at low pressures and that the presented model, in spite of its simplifications, is a valuable tool for this.

11:40am **PS-TuM11 Conformal and Anisotorpic Deposition of Cu Films using H-assisted Plasma CVD**, ***M. Shiratani***, *K. Takenaka, M. Onishi, K. Koga, Y. Watanabe*, Kyushu University, Japan, *T. Shingen*, Asahi Denka Kogyo K.K., Japan

We have developed H-assisted plasma CVD (HAPCVD),[1,2] which realizes conformal and anisotropic deposition of Cu films in trenches for Cu interconnects of small width below 100 nm. Conformal deposition is aimed at creating thin Cu seed layer for Cu electroplating, while anisotropic deposition is aimed at filling trenches completely. We have obtained the results 1-4) using fluorine(F)-free complex, $Cu(EDMDD)_2$ and the result 5) using $Cu(HFAC)_2$. The following conclusions are obtained in this study. 1) H irradiation is effective in removing impurities from the surface and inside of Cu films for a substrate temperature above 170°C. 2) Initial nucleation densities of Cu on TiN, TaN, and SiO_2 layers are above $5x10^{15}$ m^{-2} which is quite high compared to those for thermal CVD. The high nucleation density is favorable to realizing smooth thin Cu films and their strong adhesion to under-layer. 3) Deposition of Cu films of a low resistivity, 1.85 μΩcm and a

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strong adhesion above 10 MPa to TiN diffusion barrier layer has been demonstrated. Concentrations of C and O in the Cu film are much less than 0.1%, while those values at the interface between Cu and TiN are 1 and 0.2%, respectively. 4) Conformal deposition of smooth Cu films of 20 nm in thickness in trenches 0.5 μm wide and 2.73 μm deep has been demonstrated. 5) Anisotropy, which is defined as a ratio of film thickness at bottom of trench to that at its side wall, increases from 100% to 550% with increasing energy of irradiating ions from 20 V to 220 V, while H-irradiation reduces anisotropy. Promising anisotropic filling of trenches 3.5 μm wide, 2.73 μm deep has been demonstrated.

[1] M. Shiratani, et al., Sci. and Technol. of Adv. Mater. , 2, 505 (2001).
[2] K. Takenaka, et al., Proc. of Int. Symp. of Dry Process, pp.169 (2001).

Tuesday Afternoon, November 5, 2002

Plasma Science
Room: C-103 - Session PS1-TuA

Microdischarges
Moderator: M.L. Steen, IBM T. J. Watson Research Center

2:00pm **PS1-TuA1 Microhollow Cathode Discharges**[1], ***K.H. Schoenbach***, *M. Moselhy, W. Shi, R. Bentley*, Old Dominion University **INVITED**

By reducing the dimensions of hollow cathodes into the hundred micrometer range, stable, direct current, high (atmospheric) pressure glow discharges in rare gases, rare gas-halogen mixtures and in air could be generated. The electron energy distribution in these microdischarges is non-maxwellian, with a pronounced high-energy tail. The high electron energy together with the high gas density, which favors three-body collisions, is the reason for an efficient excimer generation in rare gas and rare gas-halogen microplasmas. Excimer efficiencies of up to 8% have been measured for Ar, Xe, ArF, and XeCl with a radiant excimer emittance on the order of 1 W/cm^2. Pulsing Xe discharges with 20 ns electrical pulses has led to an increase in radiant excimer emittance to 15 W/cm^2, and a simultaneous increase in efficiency to more than 20%. Operating the discharges in an abnormal glow mode has allowed us to generate microdischarge arrays without individual ballast. Stable atmospheric pressure plasmas are not only obtained with microhollow cathodes but also in electrode geometries with planar cathode, and large diameter, ring-shaped anodes, separated by approximately 100 µm. Discharges in such geometries show for pressures on the order of 100 Torr self-organized regular plasma patterns. With increasing pressure the individual plasma structures merge into a homogeneous surface plasma with similar excimer emission characteristics as that obtained with microhollow cathode discharges. Applications of these plasmas are excimer lamps, potentially micro-excimer lasers, and electron emitters.

[1]This work is supported by the NSF under Grant # CTS-0078618 and INT-0001438.

2:40pm **PS1-TuA3 Hollow Cathode Sustained Atmospheric Plasma Microjets**, ***R.M. Sankaran***, *K.P. Giapis*, California Institute of Technology

Microhollow cathode discharges (MHCDs) or microdischarges have gained recent attention for their high-pressure operation and intense UV radiation. They are normally formed between two metal foils, a cathode with a pin-hole (diameter~100 µm) and an anode of arbitrary shape. To more easily incorporate these discharges in materials processing, we have recently extended their operation to a tube geometry where gas flow can be directly coupled to the electrodes. Discharges are formed in the tube hole similar to a static case, but the flow carries the plasma outside the tube to form a microjet. In this talk, we will present features of this novel source and discuss possible applications in thin film growth and effluent gas treatment. Plasma microjets are ignited in direct current mode using a stainless steel capillary tube with a 178 µm diameter hole as the cathode and a metal grid or plate as the anode. Optical characterization has confirmed that it is necessary to shrink the hole size to below 200 µm in diameter to operate inert gases at atmospheric pressure in the hollow cathode mode. Argon microjets can be operated in ambient air at 760 Torr with voltages as low as 260 V for cathode-anode gaps of 0.5 mm. Increasing the gap and extending the plasma microjet results in an increase in the plasma voltage. The current-voltage characteristics of the plasma microjet are also influenced by the gas flow rate. For a given interelectrode distance and plasma current, increasing the flow rate reduces the plasma voltage by as much as 200 V. These effects suggest that the diffusion of air into the argon plasma stream is important. Plasma microjets offer a simple tool to perform rapid materials optimization by operating arrays of discharges. As a proof-of-concept, we have demonstrated that CH_4/H_2 plasma microjets can be used to grow diamond with fine control of the film properties by changing the gas composition.

3:00pm **PS1-TuA4 Microhollow Cathode Discharge Microreactor Chemistry**, ***D.D. Hsu***, *D.B. Graves*, University of California, Berkeley

The peak neutral temperature of a microhollow cathode discharge (MHCD) has been found from optical emission spectroscopy to be on the order of 2000 K, although adjacent temperatures rapidly drop off to near room temperature. These thermal properties suggest that MHCDs are suited to promote endothermic chemical reactions. Thin-film resistive heaters often are employed to heat reactants in microreactors. Unlike resistive heaters, the electrical power of the microdischarge heats the gas directly, offering the possibility of higher peak temperatures and greater energy efficiency. Ammonia decomposition is a highly endothermic reaction, and such a reaction could be used as a source of hydrogen for a microfuel cell. Pure ammonia was flowed through a 200 µm diameter microhollow cathode at flowrates up to 64 sccm and pressures up to atmospheric pressure. Ammonia conversion was measured by FTIR, and production of hydrogen and nitrogen was monitored by a mass spectrometer. A discharge at 490 V and 9 mA converted 16 percent of ammonia flowing at a rate of 2.5 sccm at 100 Torr. Conversion was largely dependent on the residence time of the gas in the plasma. Based on published kinetic data, the conversion and residence time data are consistent with thermal decomposition at temperatures near 3000 K. We discuss the behavior of these microplasmas as reactors for ammonia and other chemistries, and we explore methods for increasing reaction conversion.

3:20pm **PS1-TuA5 One-dimensional Simulation of Glow-like Plasma Phenomena in Parallel-plate Microdischarge Geometries**, *X. Yuan*, ***P. Kothnur***, *L. Raja*, University of Texas at Austin

Recently, microdischarges have gained much attention in the plasma process community for a variety of applications. Proposed applications range from generation of intense UV radiation to maskless etching of thin films. While some estimates of properties of microdischarge plasmas are available, a detailed understanding of the plasma dynamics and chemistry is completely lacking. This talk presents results from a self-consistent, one-dimensional computational study of the glow-like phenomena in microdischarges. A dc microdischarge in a parallel-plate geometry with gap distances of the order of 10's-100's of microns is modeled. Results for a noble gas (helium) microdischarge indicates the formation of a relatively large cathode sheath that occupies a significant fraction (~ 50 %) of the micron-sized geometry with the remaining region being the bulk plasma. The electron temperatures attain significantly high peak values (~ 50 eV) in the cathode sheath with relatively low (~ 1 eV) temperatures in the bulk plasma. Gas temperatures of ~ 1000 K and electron densities in excess of 1e14 /cm^3 are predicted. The results indicate that microdischarge plasmas are quite unique with properties that are somewhat intermediate between classical glow-discharges and thermal arc discharges.

3:40pm **PS1-TuA6 Characteristics of Miniature Microwave Excited Plasma Discharges**, ***T.A. Grotjohn***, *D. Story, S. Zuo, J.J. Narendra, A. Wijaya, J. Asmussen*, Michigan State University

Small microwave generated plasma discharges are characterized to determine their properties for discharges with sizes ranging from 0.3 mm to 10 mm and for a wide range of discharge aspect ratios. The discharge characteristics investigated included microwave power density, plasma density, electron temperature and gas temperature. The outcome of this investigation to be presented is an understanding and quantification of the microwave power density needed to operate small discharges of specific sizes, shapes, densities and gas compositions. Three microwave plasma sources are used to accomplish this investigation including (1) a highly flexible and adjustable coaxial waveguide source with the plasma generated in an adjustable gap located in the center conductor, (2) a microstrip-line based plasma source with the discharge created in a long quartz tube of 0.3 mm to a few mm in inside diameter, and (3) a microwave powered electrode system where the plasma is formed at the end of the electrode and the plasma is either unbounded or confined in a small spherical, long cylindrical or flat disk shaped chamber. The plasma compositions investigated include argon, nitrogen and hydrogen discharges. The diagnostic measurements are performed using Langmuir probes and optical emission spectroscopy. The plasma characteristics measured and modeled indicate that as the characteristic dimension of the discharge decreases to less than 1 mm, the power densities approach and exceed 1000 W/cm^3 and the plasma densities are above 10^{13} cm^{-3}.

4:00pm **PS1-TuA7 Materials with a High Secondary-electron Yield Studied in a Macroscopic Discharge Cell**, ***T.J. Vink***, *R.G.F.A. Verbeek, A.R. Balkenende, H.A.M. van Hal, S.T. de Zwart*, Philips Research, The Netherlands

Reduction of the firing voltage in plasma display panels (PDPs) calls for electrode coatings with a high secondary-electron yield. To this end we have selected a range of materials that have a low electron affinity and thus potentially a high electron emission yield. Among these materials are MgO, used as a default in PDPs, MgF_2, Al_2O_3, CsI, Rb-halogenides etc. The materials, in thin film form, were tested in a so-called macroscopic discharge cell, with dimensions that are 50 times larger than those of a discharge cell in a real PDP. Compared to the real PDP the product of pressure times electrode gap width is kept constant, and the capacitance of the dielectric layer above the electrodes is scaled accordingly. Furthermore, because of its relatively large size the macroscopic discharge cell enabled us

to prepare some of the more chemically reactive materials in situ, which is crucial for measuring surface sensitive electron emission properties properly. It is shown that the firing voltages measured in the macroscopic discharge cell compare quantitatively with respect to values obtained from a PDP test panel. A 50% reduction in the firing voltage relative to the best quality MgO can be achieved. The measured firing voltages correlate well with a relatively simple model based on ionization energy of the gas atom, and band gap and electron affinity of the solid. Finally, the occurrence of secondary-electron emission yields above the Auger limit of 0.5 are discussed in terms of ion- and photon-induced processes.

Plasma Science
Room: C-105 - Session PS2-TuA

Plasma Surface Interactions I
Moderator: K.L. Steffens, National Institute of Standards & Technology

2:00pm **PS2-TuA1 Plasma-Wall Interaction Studies during Gate Etch Processes**, ***G. Cunge***, CNRS/LTM, France, *M. Kogelschatz, N. Sadeghi*, CNRS/LSP, France, *L. Vallier, O. Joubert*, CNRS/LTM, France

During a CMOS gate etch process, requirements in terms of Critical Dimension Control are more and more severe and the process reproducibility from wafer to wafer is becoming a serious issue. Process drift are commonly observed in high density plasma sources operating in $HBr/Cl_2/O_2$ and $HBr/Cl_2/O_2/CF_4$, and originate from the deposits of SiOX and SiO-CFX layers on the reactor walls. In the present paper, mass spectrometry and optical emission have been used to investigate the influence of the reactor walls' chemical nature on the recombination rate of halogen atoms, and on the surface loss rate of silicon etch by products. To begin with, the chemical nature of the layers deposited in various chemistry has been characterized by time-resolved actinometry: after a gate etch process, the layer deposited on the reactor walls is sputtered by a pure argon plasma and the emission from etch product and halogen atoms monitored as a function of time. The results gives insight on the chemical nature of the layer as a function of its thickness. Complementary experiment where the layer is sputtered in an $Ar-O_2$ plasma also provides information on the layer deposition mechanism, which proceeds through re-deposition and oxidation of halogenated silicon etch products. As a result, we will show that when a carbon source is provided to the gas phase of an $HBr/Cl_2/O_2$ plasma (either through CF_4 addition, or in the presence of photo-resist) the layer composition change from SiOCl to a mixture of SiOCl-C(F) species. Mass spectrometric measurement demonstrates that the presence of carbon in the layers is accompanied by a drastic increase of the Br and Cl atoms recombination coefficient, whose concentration in the gas phase consequently drops.

2:20pm **PS2-TuA2 Effect of Plasma Chamber Wall Conditions on Atomic Chlorine Concentration and Polysilicon Etch Rate Uniformity**, ***T.W. Kim****, *E.S. Aydil*, University of California, Santa Barbara

The effect of reactor wall conditions on atomic chlorine concentration and polysilicon etch rate uniformity was studied in a high-density inductively coupled plasma reactor. Experimental measurements of etch rate and two dimensional ion flux distributions on the wafer are combined with a simple transport and reaction model for Cl atoms in the plasma to elucidate the effect of reactor wall conditions on the etch rate uniformity. Specifically, we focus on the effects of wafer-to-wafer drifts from the wall conditions and effects of such drifts on the uniformity of etching. The spatially averaged etch rate across the wafer surface increases with time as etch products react with residual oxygen in the chamber and coat the reactor walls with a thin layer of silicon oxychloride film. Etch rate is highest at the center of the wafer when the anodized aluminum reactor walls are maintained in a "clean" state, free of silicon oxychloride deposits. In contrast, the etch rate peaks at the edges of the wafer with a local maximum near the pumping port when the reactor walls are coated with the silicon oxychloride film. The spatially averaged ion flux increases slightly while ion flux uniformity does not change as the reactor walls are covered with the silicon oxychloride film indicating that the drift in etch rate and etch uniformity is primarily due to the drift in atomic chlorine concentration and its spatial distribution. The increase in atomic chlorine concentration is due to its lower recombination probability on the silicon oxychloride film surface as compared to the "clean" anodized aluminum wall. As the reactor walls are coated with the silicon oxychloride film the etch rate distribution changes from a center-fast profile to a edge-fast profile due to a change in the dominant atomic chlorine depletion mechanism from wall recombination to recombination on the wafer surface.

2:40pm **PS2-TuA3 Abrupt Changes with Mixture Composition in the Surface Coverage and Etch Rate During Si Etching by Cl_2-Ar Plasmas**, *N.C.M. Fuller*, ***I.P. Herman***, Columbia University, *V.M. Donnelly*, University of Houston

Laser desorption of the adlayer, with laser-induced fluorescence and plasma-induced emission detection of the desorbed adsorbates, has been used to investigate Si etching in inductively coupled Cl_2-Ar plasmas. These techniques show that the relative coverage of $SiCl_x$ species and etch rate increase and the coverage of Si decreases very abruptly as the chlorine fraction is increased for a 75% Cl_2 plasma with the bias set for 80 eV ions. The Cl_2 fraction required to produce this abrupt change increases with an increase in ion energy. There is no corresponding abrupt change in the Cl, Cl^+, and Ar^+ densities or electron temperature at this mixture condition, as measured by optical emission spectroscopy. The implications of these results and the reaction mechanism will be discussed. This work is supported by NSF Grant No. DMR-98-15846.

3:00pm **PS2-TuA4 Generating High-efficiency Neutral Beams by Using Negative Ions in an Inductively Coupled Plasma Source**, ***S. Samukawa***, *K. Sakamoto*, Tohoku University, Japan, *K. Ichiki*, Ebara Research Co., Ltd., Japan

To minimize radiation damage caused by charge build-up or ultraviolet and x-ray photons during etching, we developed a high-performance neutral-beam etching system. The neutral-beam source consists of an inductively coupled plasma (ICP) source and parallel top and bottom carbon plates. The bottom carbon plate has numerous apertures for extracting neutral beams from the plasma. When a direct current (DC) bias is applied to the top and bottom plates, the generated positive or negative ions are accelerated toward the bottom plate. Most of them are then efficiently converted into neutral atoms, either by neutralization in charge-transfer collisions with gas molecules during ion transport and with the aperture sidewalls in the bottom plate, or by recombination with low-energy electrons near the end of the bottom plate. We found that negative ions are more efficiently converted into neutral atoms than positive ions. The neutralization efficiency of negative ions was almost 100%, and the maximum neutral flux density was equivalent to 4.0 mA/cm^2. A neutral beam can thus be efficiently produced from the ICP source and apertures in our new neutral-beam source.

3:20pm **PS2-TuA5 Direct Detection of Radical and Stable Species Impacting and Desorbing from Surfaces**, ***Y. Kimura***, *J.W. Coburn, D. Fraser, D.B. Graves*, University of California, Berkeley

We present results from a new vacuum beam apparatus that has been designed to measure directly the radical and stable species fluxes impacting surfaces and the products that form as a result of these interactions under high vacuum conditions. The Radical- and Ion-Surface Interaction Analysis System (RISIAS) is equipped with an external plasma source that creates a beam of radicals, and a threshold ionization quadrupole mass spectrometer (TIQMS) that is aligned with the beam's line of sight. This setup allows us to measure all the radical and stable species in the beam. The TIQMS is vertically translatable to allow a horizontal insertion of a sample surface into the beam path via a load lock. With the sample surface in place, all species desorbing from the surface can also be detected with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and product components. The addition of ion bombardment from a separate ion source on the chamber before or during radical beam exposure allows us to simulate processes with substrates in direct contact with a plasma. We demonstrate operation of RISIAS with O, N, NH, and F radicals impacting a variety of surfaces. In particular, we report the etch product composition for a nanoporous silica film (hydrogen silsesquioxane, or HSQ) etched with fluorine. The products include SiF_4, SiH_4, O_2 and a variety of carbon-containing species, apparently due to carbon contamination in the film.

4:00pm **PS2-TuA7 Film Formation, CF_2 Reactivity and Ion Effects in Fluorocarbon Plasma Systems**, ***I.T. Martin***, *E.R. Fisher*, Colorado State University

Fluorocarbon plasmas are widely used for the deposition of fluoropolymer films possessing a variety of useful properties, such as hydrophobicity, chemical inertness, and low surface energies. Ions play an important role in plasma film deposition, either as precursors to film deposition or as bombarding species that sputter or cross-link the depositing film. In order to better understand the mechanisms of film formation, gas phase and gas-surface interaction studies are combined with the results of the characterization of films deposited from C_3F_8 and C_4F_8 plasmas. Plasma Ion-Mass Spectrometry (PI-MS) is used to identify nascent ions in the

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plasma systems at different RF powers, which can then be linked to film structures and reactivity measurements. Plasma conditions that minimize the formation of ions lead to the deposition of less cross-linked fluorocarbon films; conditions that enhance fragmentation of the parent gas lead to higher deposition rates within the plasmas. In addition to film characterization, we have used our Laser Induced Fluorescence (LIF) based imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF_2 molecules with Si substrates during plasma processing. CF_2 surface loss coefficients determined for 25-100 W C_3F_8 and C_4F_8 plasmas show relatively high levels of scattering, which indicates that CF_2 molecules are produced at the surface in these systems. Overall, scatter coefficients measured in the C_4F_8 system are higher than those measured in the C_3F_8 system. These data are correlated with the identity of the nascent ions in the plasma systems. Results for ion free conditions are also discussed. Collectively, the data presented provide a fairly comprehensive picture of these fluorocarbon systems, from the gas-phase to the material to the plasma-surface interface.

4:20pm **PS2-TuA8 Surface Reaction Analyses for Si/SiO_2 Selective Etching Processes using Molecular Dynamics Simulations**, ***S. Hamaguchi***, Kyoto University, Japan **INVITED**

Molecular dynamics (MD) simulations are used to study surface reaction dynamics during dry etching processes of Si and SiO2 surfaces. First simulation results of Si and SiO2 etching by Cl and F beams are presented. In these processes Si is selectively etched over SiO2, the mechanism of which can be easily understood from the observation of surface conditions obtained from MD simulations. We also discuss the difference between beam etching and plasma etching (where a large number of low-energy charge-neutral reactive species exist) for these processes. Secondly we present simulation results of SiO2 etching by CxFy. Thirdly enhanced surface diffusion effects by relatively low-energy ion bombardment (the energy of which is below etching threshold) are presented. To perform these MD simulations, we have developed classical interatomic potential functions using potential energy data obtained from ab initio calculations of electronic states for various molecules and radicals. To model Si and SiO2 etching by halogens, we have constructed Stillinger-Weber type potentials for Si-O-Cl and Si-O-F systems. The potential functions for SiO2 and Si etching by CxFy, are of hybrid type of Stillinger-Weber type functions and Abell-Tersoff-Brenner type functions. The details of these potential functions are also discussed in the presentation.

5:00pm **PS2-TuA10 Subsurface Diffusion and Reaction of Fluorine Atoms in Photoresist**, ***F. Greer***, *D. Fraser, J.W. Coburn, D.B. Graves*, University of California, Berkeley

Radicals created in plasmas are known to play important roles in thin film etching, deposition, cleaning, stripping and surface modification. The present study is aimed at developing a more quantitative model of radical-surface interactions. Room temperature measurements of F atoms abstracting D atoms from a deuterated photoresist surface to form DF were made in a vacuum beam apparatus, with simultaneous monitoring of film mass change with a quartz crystal microbalance. These measurements were interpreted as abstraction of D by F, followed by F saturation of dangling bonds previously occupied by D. However, the rate of DF formation and mass uptake due to F saturation showed a relatively long-lived tail, inconsistent with surface-only reactions. After the initial stage, subsequent DF formation and mass uptake appeared to be limited by F atom diffusion into the sub-surface since the measured rate of mass change and DF flux from the surface both varied inversely as $t^{1/2}$. The surface abstraction probability of D by F was inferred to be 0.25, and the value of the F atom diffusivity was consistent with values reported for diffusion in polymers. These results will be discussed in terms of studies with other halogen radicals as well as nitrogen radicals. The application of these results to atomistic scale models of plasma etching will also be discussed.

Plasma Science
Room: Exhibit Hall B2 - Session PS-TuP

Plasma Applications

PS-TuP1 Temperature Mapping in Fluorocarbon Plasmas using PLIF of CF, ***K.L. Steffens***, National Institute of Standards and Technology

During semiconductor processing, fluorocarbon plasmas are commonly used for dielectric etching. As model-based reactor design and process development become more prevalent, data is needed for model development and validation. The translational temperature in a plasma can vary spatially, leading to spatial variations in gas density and reaction rates. Spatial mapping of these temperature variations would provide useful information for modelers. In this work, 2-D temperature maps in fluorocarbon plasmas, measured using planar laser-induced fluorescence (PLIF) of the CF radical, will be presented. Measurements are made in the capacitively-coupled Gaseous Electronics Conference rf Reference Reactor in CF_4 plasmas at various power levels at 200 mTorr. PLIF has previously been used to measure spatial maps of CF_2[1] and CF radicals in fluorocarbon plasmas, by exciting the species with a laser sheet and imaging the fluorescence using an intensified CCD camera. In this variation of the PLIF technique, multiple spatial maps are imaged for the same plasma, exciting a different rotational line of the CF radical for each image. The fluorescence intensity map in each image is related to the rotational population in the probed CF ground state rotational level. Assuming a Boltzmann distribution, the ratio of image intensities can used to calculate the rotational temperature of CF, which is expected to be in equilibrium with the plasma's translational temperature under these conditions.

[1] K. L. Steffens and M. A. Sobolewski, J. Vac. Sci. Technol. A 17(2) 517 (1999).

PS-TuP2 A Comparison of the Performance Between Low Pressure Magnetized and Non-magnetized Microwave Discharges, *M. Perrin, T.A. Grotjohn,* ***J. Asmussen***, Michigan State University

Microwave discharges can be created and maintained at low pressures both with and without the application of static (ECR and non-ECR) magnetic fields. Thus important microwave plasma source design issues are (1) when is the application of a static magnetic field advantageous, (2) what are the differences between the output performance of similar magnetized and non-magnetized microwave discharges, (3) what microwave heating mechanisms maintain the two different microwave discharges at low pressure? This investigation attempts to answer these questions by experimentally measuring the performance of a 13cm diameter microwave plasma source operating in argon gas from 1-50 mTorr with and with out a set of multipolar permanent magnets. Specifically, differences between magnetized and non-magnetized discharges are noted by comparing measured electron densities, electron distribution functions and effective electron temperatures versus pressure,i.e. 2-50 mTorr, and absorbed microwave power from 200-500W. The discharge stability of each configuration is also noted. The experimental results indicate that at pressures above 6 mTorr the non-magnetized discharge is superior in all aspects of performance to the magnetized discharge. Thus above a specific pressure ;i.e. 6 mtorr in this case, the application of static magnetic fields is not required to efficiently maintain microwave plasma processing sources. In fact the application of a magnetic field may reduce source efficiency. However at very low pressures ,i.e.below 4mtorr in this case, magnetized discharges are more efficient and stable and have lower electron temperatures and plasma potentials. The experimental measurements suggest that the non-magnetized discharge is maintained by non-collisional mechanisms at pressures below 15-20 mTorr. The similarity between discharge configurations also then suggests that similar non-collisional heating mechanisms are present in the magnetized discharge.

PS-TuP3 Ion Attachment Mass Spectrometer(IAMS) for in situ and Fragment-free Monitoring of Plasma-CVD and Dry-etching Processes, ***Y. Hirano***, *M. Nakamura, Y. Shiokawa, T. Fujii,* Anelva Corporation, Japan

We have developed and commercialized Ion Attachment Mass Spectrometer (IAMS),[1] which supplies mass spectra with no peaks due to fragment ions. Molecular ions are observed in spectra of even reactive molecules such as radicals. We demonstrated that IAMS enabled us to detect molecular ions of reactants of the Cu-CVD process and PFCs(perfluoro compounds) in an exhaust gas from a dry etching machine.[2] However, our spectrometer shows the highest sensitivity at the sample pressure of 100 Pa so far and is hardly applicable to the in situ measurements of gases for etching or CVD whose pressure is less than 10 Pa; where signal intensity for the sample at a pressure of 1 Pa was roughly estimated to be 10,000 times smaller than at the pressure of 100 Pa. In this study, we have improved the IAMS as to show the satisfactory sensitivity for the sample with the pressure of 1 to 10 Pa by (1)decelerating primary ions before collision with sample molecules, and (2)improving efficiency of transportation of ions by using a specially designed ion lens system. As a result, the peak due to molecular ion for neat cyclo-C_4F_8 was observed at a pressure of 1 Pa where the signal intensity of $2X10^{-8}$ A and S/N of 10^4 were obtained at the SEM gain of 10,000. The low-Pressu re-IAMS has been found to be useful for in situ fragment-free monitoring of molecules and radicals, especially in plasma -CVD and dry etching processes. Precious discussions with Prof. Munetaka Nakata and Prof. Masao Takayanagi of Tokyo University of Agriculture and Technology are gratefully acknowledged.

[1] T.Fujii, Mass Spectrometry Review 19(2000)111.
[2] M.Nakamura et al JVST-A 19(2001)110 5.

PS-TuP4 Sub-Millimeter Absorption Spectroscopy of Fluorocarbon Plasmas, ***E.C. Benck***, National Institute of Standards and Technology

Sub-millimeter (300 GHz to 1 THz) absorption spectroscopy is being developed as a diagnostic for measuring radical densities and temperatures in processing plasmas for microelectronics. Most molecules, radicals, and ions have transitions suitable for detection at these frequencies and the necessary spectroscopic data is available in the literature for determining the absolute radical densities. In addition, the narrow linewidths of < 10 kHz of these continuous-wave 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 density measurements have been made in inductively and capacitively coupled GEC Reference Reactors. The influence of wafer coatings on plasma chemistry has been measured for several different fluorocarbon (C_4F_8, C_4F_6, and C_5F_8) / oxygen etching gas mixtures.

PS-TuP5 Neutral Gas and Positive Ion Species of Ar/SF6 Inductive Plasma Discharges, ***R.R. White***, *M. Tuszewski,* Los Alamos National Laboratory, *A.M. Marakhtanov,* University of California, Berkeley

The neutral gas and positive ion species of Ar/SF6 inductive plasma discharges are studied with a Balzers PPM421 mass spectrometer. The species of two inductive plasma sources are compared: (1) a hemispherical plasma source operated at 0.46 MHz and, (2) a planar plasma source operated at 13.56 MHz. No Faraday shield is used between the coil and the quartz dielectric. The capacitive coupling of the hemispherical source is much smaller than that of the planar source. The radiofrequency (rf) power is varied between 0 and 1 kW, the gas pressure is varied between 1 and 10 mTorr, and the SF6 gas concentration is varied between 0 and 1. The main results obtained so far with the hemispherical plasma source are listed below. The SF6 gas is largely dissociated into fragments such as SF and SF2. These gas fragments have relatively low (10 - 12 eV) ionization potentials that are important for discharge sustainment. Dissociation fractions up to 95% are observed for the lowest pressures and for the highest rf powers. SF3+ is found to be the dominant positive ion species for most discharges. However, the SF5+, SF2+, and SF+ ion concentrations are significant at the lowest gas pressures and highest rf powers. Impurity gas and ion concentrations are relatively low for most discharges. Similar data acquired with the planar source will be presented and compared to those of the hemispherical source.

PS-TuP6 Introduction of a Powerful New Method of Generating Accurate Endpoint Traces Combined with Process Fault Classification for Low Dimensional Open Areas, ***D. Knobloch***, *F.H. Bell,* Infineon Technologies AG, Germany, *K. Voigtlaender, J. Zimpel,* ADP GmbH, Germany

A powerful new method of generating accurate endpoint traces based on full range optical emission spectroscopy (OES), e.g. for contact hole and VIA etch, is presented. Conventional endpoint systems derive endpoint signals by monitoring one or two discrete wavelengths. However, this technique is not accurate enough for logic and advanced memory products with low open areas and highly topographical structures. Consequently, more sophisticated and robust endpoint control of plasma processes requires the use of the full optical spectral information and powerful analysis methods. Statistical methods based on algorithms, such as evolving windows factor analysis (EWFA), principal component orientation (PCO), Hotelling's T2 and others have been used to find suitable endpoint traces. However these methods do not tend to be robust enough, because all changes in plasma emission - not only endpoint relevant changes - will be traced. To overcome these problems, a newly developed algorithm that

separates endpoint information from process faults and variations is presented. The algorithm uses the complete individual weighted spectral endpoint information for a long-term robust and sensitive endpoint detection. The algorithm is based on modelling techniques constructing an optimal superposition of spectral eigenvectors to generate a spectral software filter. The application of this method in the production works like a black box for the engineer. The only requirement is the predefinition of the shape of the expected endpoint trace. Accurate and robust endpoint detection of open areas beyond 0.5% and highly topographical structures is achieved and presented.

PS-TuP7 Laser Thomson Scattering Diagnostics of Plasmas near Material Surfaces, *K. Muraoka, K. Uchino, Y. Yamagata,* ***Hassaballa Safwat***, Kyushu University, Japan

Laser Thomson scattering is a well established technique for measuring electron density and temperature of high temperature plasmas. During the last decade, the applicable range of the technique has been expanded to measurements of electron properties, not only electron temperature and density, but more generally eedf itself, of glow discharge plasmas by using data accumulation and photon counting technique.[1] It is presently being further expanded to diagnose plasmas near material surfaces of less than 100 microns. This should enable us to study plasmas of interest for barrier discharges used for plasma display panel. In addition, this will make possible to study, for example, cathode sheath phenomena, where electron drifts away from the cathode should be directly detectable. The potential of this new development is discussed.

[1]K. Muraoka et al., Plasma Sources Sci. Technol. (to be published).

PS-TuP8 Study of Process Variables and Plasma Parameters during Reactive Sputtering from a Titanium Hollow Cathode Source, ***A. Pradhan***, *S.I. Shah*, University of Delaware

Hollow Cathode Sources offer the advantages of conformal depositions and high target utilization and the ability to coat three-dimensional objects over planar sources. In addition, we have found that Hollow Cathode Sources are more suitable for reactive sputtering of compound materials as they offer stable operation and significantly higher deposition rates. These advantages have been demonstrated by using a titanium Hollow Cathode Source to reactively deposit titania thin films. The target potential and current did not exhibit the hysteresis commonly observed with planar sources. Target charging and the related arcing was not observed, even on the increasing the oxygen concentration in the sputtering gas past the metal-oxide transition point. Thin films were deposited on glass substrates and characterized by XPS and XRD. In addition, Langmuir probe measurements were carried out to determine the variation of the plasma parameters with oxygen concentration in the reactive gas and time. The spatial variation in the plasma parameters was also determined by moving the probe along the long axis of the Hollow Cathode. The electron temperature was close to 1eV, and the plasma potential varied from a few volts below to a few volts above zero. The plasma density was orders of magnitude greater than that obtained in planar sputtering, which would help explain the high deposition rate observed.

PS-TuP9 On the Limits of Operation of a Species-selective Gauge Based on the Penning Discharge Configuration[1], ***C.C. Klepper***, *R.C. Hazelton, F. Barakat, J. Niemel, M.D. Keitz,* HY-Tech Research Corporation, *J.P. Verboncoeur,* University of California, Berkeley

A Penning discharge tube has been used as the excitation source for optical detection of gaseous species concentrations in a neutral gas. This type of diagnostic has been primarily used in magnetic fusion energy experiments for the detection of minority species in the effluent gas (e.g. for helium detection in a deuterium background). Recent innovations[2] have allowed for extension of the operation range from <1Pa to as high as 100Pa and possibly beyond. This is done by dynamically varying the gauge parameters to keep the optical signals nearly constant (or at least away from a non-linear dependence on the pressure). However, there are limitations to this approach, because the Penning discharge can manifest itself in a number of modes, each exhibiting a different spatial emission pattern. As a result, varying the discharge parameters can cause the gauge to undergo transitions between these modes, disrupting any intended monotonic dependence of the overall emission on the varied parameter and hence any predicable impact on the emission. This paper discusses some of the modes observed experimentally. It also presents some progress made to date in using a particle-in-cell (PIC) code to predict these modes and mode transitions. The hope is that a good understanding of the physics involved in the mode transitions may allow for methods of either avoiding or suppressing such modes. This would aid in broadening the use of this plasma-based sensor technology.

[1] Research sponsored in part by the US Department of Energy under contract # DE-FG02-98ER82592-A001 (Phase II SBIR) with HY-Tech Research Corporation.

[2] C.C. Klepper et al., "Species-selective pressure gauge with extended operation", US Patent No.6351131, granted Feb. 26, 2002

PS-TuP10 A Comparison of Techniques for Measuring Plasma-induced Damage, ***P. Sakthivel***, *A. Srivastava, M. Colson, M. Tun*, Axcelis Technologies, Inc.

Plasma-induced damage is a key parameter that directly affects yield in chip manufacturing, and is even more critical for the new technology nodes that the semiconductor industry is poised to tackle. While many techniques have evolved to characterize the level of plasma damage at different stages of exposure to plasma during the manufacturing process, no single technique is considered uniquely reliable. We present, in this paper, a comparison of three of the most sensitive techniques for characterizing the performance of a second generation 300mm downstream microwave plasma strip system, the FusionES3i. The ES3i has nearly double the input microwave power for its upstream plasma source as its predecessor, and an additional RF Assist capability-a radio frequency capacitive source designed to provide low energy ions on demand. High density maps of contact potential difference were obtained on oxide coated silicon wafers to assess charging of the oxide layer on the asher using the COCOS technique (SDI), and compared with maps produced by the COS technique(KLA). NMOS and PMOS devices with several antenna ratios were also fabricated at International SEMATECH and exposed to the plasma under typical ash conditions, to compare the sensitivity of this technique to the two non-contact techniques. During some of the tests, both the upstream microwave and RF sources were operated simultaneously. The different techniques indicated that there was no evidence of charge damage for even "long" processes like post-implant strip, during which low energy ion bombardment could be used in conjunction with the microwave source. The spatially resolved data also provided a picture of the uniformity in distribution of ions over the surface of the wafer.

PS-TuP11 Electron Energy Distribution Function Measurement in Dual Frequency Very Narrow Gap Capacitively Coupled Plasma, ***B.I. Jeon***, *H.Y. Chang*, Korea Advanced Institute of Science and Technology (KAIST)

We measured Electron Energy Distribution Function(EEDF) in very narrow gap dual frequency Capacitively Coupled Plasma(CCP). 2Mhz and 27Mhz dual radio frequency is used. Electrode gap is variable bewteen 13mm and 24mm. To get the reasonable EEDF noise suppression is indispensible. We made self resonant coil with resonant frequency 2, 4, 27 and 54 Mhz to reduce rf noise. We use pulse measuring technique(double differentiation method) to get EEDF. Proper design of probe, rf noise seppression coil and low-pass filter in double differentiation circuit, we can measure EEDF in noisy plasma.

PS-TuP12 Plasma Characteristics of Magnetically Confined Linearly Extended Inductively Coupled Plasma, ***B.K. Song***, *Y.J. Lee, C.H. Jeong, G.Y. Yeom*, Sungkyunkwan University, Korea

Development of large-area high-density plasma sources is desired for a variety of next-generation plasma processing from microelectronic device fabrications to high resolution flat panel display(FPD). The plasma source developed for these application includes surface wave plasmas, inductively coupled plasmas, etc. In these plasmas, however, problems in conjunction with electron energy such as SiO_2/Si etch selectivity, etc. have been reported. These are related to the fact that the high energy portion of the electrons are prone to be exceedingly energetic in high density plasmas generated especially at low pressure and cause inadequate radical/ion ratio in the plasma. In this study, parallel-connected linear inductive antenna designs have been used to generate inductively coupled plasmas and, to improve both the plasma density and the electron temperature control, multiple-cusp magnetic fields employing permanent magnets were used and the effects of various magnet combinations and process conditions on the plasma characteristics were studied. The permanent magnets having 3000G on the magnet surface were arranged above the parallel-connected linear copper antennas by varying center-to-center distance of the magnets. Plasma characteristics such as electron temperature, ion density, and electron energy distribution functions were measured by a Langmuir probe as a function of with/without multiple-cusp magnetic confinement at low pressure Ar plasmas. The use of optimized multiple-cusp magnetic confinement in the parallel-connected linear inductive antenna designs showed improved electron temperature control in addition to the increase of plasma density. QMS(Hiden Analytical Inc., PSM 500) and OES(SC technology., PCM 402) measurement were also carried out to characterize the plasmas for the parallel-connected linear inductive antenna designs with/without the multiple-cusp magnetic confinement.

PS-TuP13 Large Area Plasmas Processing System Based on Electron-Beam Ionization, ***D. Leonhardt***, Naval Research Laboratory, *S.G. Walton, D.D. Blackwell,* SFA, Inc., *R.F. Fernsler, R.A. Meger*, Naval Research Laboratory

Electron beam (e-beam) ionization has been shown to be both efficient at producing plasma and scalable to large area (square meters). NRL has developed a 'Large Area Plasma Processing System' (LAPPS)[1] based on the e-beam ionization process, with the goals of increased control over plasma-to-surface fluxes and the modification of materials surface properties over large areas. Our system demonstrates that the beam ionization process is fairly independent gas composition and capable of producing low temperature plasma electrons in high densities. The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2-5kV, ~ 1 mA/cm^2 electrons injected into a neutral gas background (oxygen, nitrogen, sulfur hexafluoride, argon). Typical operating pressures range from 20-200 mtorr with beam-collimating magnetic fields (100-300 Gauss) for plasma localization or without magnetic fields for a more diffuse, volumetric plasma source. Time-resolved in situ plasma diagnostics (Langmuir probes, microwave transmission and mass spectrometry) will be shown to illustrate the low electron temperature (<1eV), high electron densities (10^9-$10^{13}cm^{-3}$) and plasma-to-surface fluxes. Emphasis will be placed on recent surface modification tests consisting of silicon etching, anisotropic removal of polymeric material (photoresist) and organic surface activation for multi-step large-area applications. Plasma chemistry issues associated with modifying these materials using different feedstock gases in these plasma sources will be presented. In particular, the capability of high degree of dissociation and control over the incident ions will be discussed. These results come from plasma sheets in various test systems, with active areas ranging from 15cm x 20cm to areas approaching 1 square meter. Substrate uniformity in larger sources will also be discussed.

[1] Work supported by the Office of Naval Research.

PS-TuP14 Large Area Surface Modification by Atmospheric Pressure Plasma for Cleaning and Adhesion, ***Y.H. Lee***, *C.H. Yi,* SungKyunKwan University, Korea, *E.S. Choi,* LG-PRC, *H.C. Woo,* Korea Vacuum Tech., *G.Y. Yeom*, SungKyunKwan University, Korea

Plasma treatment for surface modification has been used to produce hydrophobic or hydrophilic surface on metals, plastics, glass, or polymers in industry. Especially, due to the possible low capital cost of ownership, simplicity, high throughput, etc. plasma surface treatment under atmospheric pressure is actively studied, currently. In this study, a novel large area atmospheric pressure plasma apparatus has been used to generate a large area atmospheric pressure plasma (plasmas larger than 700mm in width) and the effects of this type of plasma apparatus on the removal of organic material of large area glass substrates, ITO/glass, and Ag/ITO/glass for the large area display panel such as TFT-LCD panels and plasma display panels have been carried out. A low frequency AC power supply with a sine wave voltage (3-100kHz) was used to generate the plasmas under atmospheric pressure. He was used as the ignition and discharge gas and O_2 was used as the reactive gas. He/O_2 plasmas were generated between the two electrodes covered with a dielectric having slot shape holes and facing each other at a distance of a few mm. The sample was mounted just below the plasma region formed by these two electrodes. The size of the electrodes was 20mm(L) x 760mm(W). Using this type of atmospheric pressure plasma apparatus, dense, uniform, and very stable plasma could be obtained on the entire area of the electrode. Using this apparatus, organic materials such as photoresist were etched to estimate the cleaning rate of organic materials and cleaning uniformity. Characteristics of the plasmas were investigated by I-V characteristics using a current probe and a high voltage probe and by optical emission spectroscopy and cleaning rate was measured using a step profilometer. Characteristics of the cleaned sample surface were investigated by X-ray photoelectron spectroscopy and also by measuring contact angle of water drops.

PS-TuP15 Microwave Power Coupling Principles for Generating Small Microwave Plasmas, ***S. Zuo***, *J.J. Narendra, A. Wijaya, D. Story, T.A. Grotjohn, J. Asmussen*, Michigan State University

The development of small high density (10^{12} -10^{13} cm^{-3}) microwave plasma sources with dimensions of 0.3 mm to several mm are under investigation. These mini plasma sources can be generated and sustained by either capacitive coupling of the microwave fields to the discharge or by a plasma resonance coupling to the discharge. Further, in some configurations plasma guided waves can be generated that power the discharge along an extended length. Various microwave field generating structures have been investigated including discharges created in the gap in the center conductor of a coaxial waveguide/cavity structure, discharges created in a quartz channel located in the dielectric layer of a microstripline, discharges created in the gap of the metal line of a microstripline, and discharges created at the end of a microwave powered electrode. The discharges generated by each of these configurations have been characterized to assess the power coupling characteristics and efficiencies of these various structures. These microwave power coupling structures have also been analyzed using electromagnetic field simulation tools. Additionally, the microwave fields in the structures that generate plasma guided waves have also been characterized using a very small sampling antenna along the plasma. The structure of these plasma guided waves have been analyzed for both long linear plasmas and for plasmas that branch into Y or T shapes using experimental measurements and electromagnetic/plasma models.

PS-TuP16 Simulation of a Micro-Plasma Reactor, *D. Economou*, ***S.K. Nam***, University of Houston

Recently, there has been interest in microfabricated plasma reactors with potential uses in ion thrusters, plasma displays, as integral parts of microelectromechanical systems (MEMS), etc. We have developed a self-consistent simulation model to study microfabricated inductively coupled plasma reactors. The Maxwell equations provide the power deposition profile; this is used in an electron energy equation to predict the electron temperature (assumed Maxwellian EEDF) and the rate coefficients of electron-impact reactions. These are in turn used in ion and neutral species balances to predict their 2-D density profiles. The simulation evolves until convergence. We have studied an argon plasma in a micromachined ICP, including the effect of metastables. Results will be shown and analyzed in view of the large surface-to-volume ratio of the micro-plasma reactor. Simulation results will be compared with the data of Hopwood et al (JVST B, vol. 18, p. 2446, 2000). Work supported by the NSF.

PS-TuP17 Affecting Plasma Polymerised Film Properties by the Control of Ion Energy, ***D. Barton***, *R.D. Short,* University of Sheffield, UK, *J.W. Bradley*, UMIST, UK

By applying an RF potential onto a substrate, which is matched in phase and amplitude to these potentials in the plasma, we are able to selectively control the ion energy distribution function at a depositing surface. This technique does not perturb the bulk plasma, and therefore leaves other particles incident on the substrate, e.g. radicals, excited species, unaffected. Because of this, we are able to estimate, in-situ, the effect of ion energy upon film structure and properties. We have incorporated a suite of diagnostics including deposition rate monitor, an energy resolving mass spectrometer and an ion flux probe. Deposited films were examined ex-situ using XPS and SIMS techniques. We present data for the different monomer types triglyme and acrylic acid, and demonstrate that ion energies affect both the deposition rate, and introduces new functionalities onto the film surface.

PS-TuP18 Study of Continuous Fluorocarbon Ion Deposition on Polystyrene Surfaces using Molecular Dynamic Simulations, ***I. Jang***, *S.B. Sinnott*, University of Florida

In this study, continuous deposition of polyatomic fluorocarbon ions ($C_3F_5^+$) on polystyrene surfaces is investigated using molecular dynamics simulations. The forces are determined using the reactive empirical bond order method for short-range interaction and Lennard-Jones potential for long-range van der Waals interaction. The incident energy of the ions is 50 eV and the incident angle is normal to surface. The results predict that 47.2 % of carbon atoms and 47.7 % fluorine atoms from incident ions are deposited on the surface. Major species remaining on the surface are the intact ion ($C_3F_5^+$) and CF_2 fragments. The average penetration depth of the ions and fragments is 1.7 nm. Some surface etching occurs during the deposition process. On average, one carbon and hydrogen atom is removed from the surface for every second ion that is deposited. Some ions or fragments combine with each other and form larger molecules. Thus, the simulations document the atomic-scale processes that ultimately lead to the growth of fluorocarbon thin films.

PS-TuP19 Ion Energy Distributions at the Substrate and Feature Charging During Plasma Etching, ***A.E. Wendt***, *R. Silapunt, M. Patterson, R. Ding, Y.-H. Ting*, University of Wisconsin - Madison

Substrate bombardment by energetic ions is a critical element of many plasma processes, and the magnitude of the ion energy is an important process parameter. However, the conventional sinusoidal bias voltage waveform generally leads to broad bimodal ion energy distributions (IED) at the substrate, and therefore cannot be used to take full advantage of ion bombardment as a means of controlling process results. By using a non-sinusoidal bias voltage waveform, we are able to produce a narrow IED at the substrate, with dramatic results that may help in meeting future IC manufacturing requirements. Our tailored bias voltage waveform has a periodic shape at the substrate consisting of a short spike in combination with a longer period of constant voltage. Most ions cross the sheath during the period of constant sheath voltage, resulting in a narrow IED. The height of the spike sets the magnitude of the ion energy. We have previously

reported measurements of the sheath voltage waveform and etch selectivity on blanket films, confirming the effectiveness of this approach. This paper addresses the influence of the IED on feature charging during the etching of patterned dielectric films. In contrast to blanket films, in high-aspect-ratio features there is a greater shadowing effect for electrons than for ions. As a result, the feature bottoms will charge positive and deflect ions, and a steady state is reached when electron and ion fluxes balance. A limitation of a narrow ion energy distribution in that case is that the feature bottom must charge to a much higher potential in order to deflect the ions compared to the case of a bimodal distribution that includes some low energy ions, drastically reducing the energy of the remaining ions that do reach the feature bottom, affecting selectivity and etch rate. Proposed modifications of the tailored voltage waveform to address these issues will be presented.

[1] Supported by SRC and NSF ECS-0078522.

PS-TuP20 Energetic CF_3^+ and F^+ Bombardments of Si Surfaces using Molecular Dynamics Simulations, ***J.J. Seo***, *J.W. Kang, H.J. Hwang*, Chung-Ang University, Korea

Classical molecular dynamics (MD) simulations for Si etching by energetic fluorocarbon and fluorine ions have been performed to study surface ion reaction mechanisms for plasma etching. The Si-C-F potential function developed by Abrams and Graves was used to describe surface-atom interaction, which is based on the tersoff formalism. When CF_3^+ ions impacted sequentially on a Si substrate with incident energies of 50, 100 and 200 eV at normal incidence, we have observed that a mixed layer of CF_3^+ ions and Si is formed on the surface. Our results also showed that the thickness of F coverage increases and then it is saturated, as the Si surface is irradiated with F^+ ions. Etch rates and selectivities obtained from MD simulations was compared with available experimental data and another simulation result.

PS-TuP21 Simulations of Topography Defects Development (Undercut and Bowing) for Deep Silicon Etching under a SF_6/O_2 Plasma Chemistry, ***G. Marcos***, University of Orleans, France, *A. Rhallabi*, University of Nantes, France, *P. Ranson*, University of Orleans, France

New microelectronic applications such as MicroElectroMechanical Systems (MEMS) need very high aspect ratio trenches (deep/width>60) in semiconductors. Improvements in dry etching processes have been performed in obtaining deep silicon trenches by using a cryogenic method in an Inductive Coupled Plasma reactor with a SF_6/O_2 plasma discharge(see abstract of M. Boufnichel at al). The experimental research has shown that undercut and bowing formation is strongly correlated with plasma parameters, mask shape and time during processing. In order to understand the involved plasma-surface interaction mechanisms, we have developed a two dimensional etching model based on Monte-Carlo techniques. This etching model includes different surface processes due to neutral reactive species such as the fluorine and the atomic oxygen. Their flux is assumed to be isotropic. A transport model through the RF sheath is connected with the surface model to calculate angular and energetic ion function distribution. Monte-Carlo approach allows to introduce physical processes with probabilistic considerations, such as adsorption/desorption, spontaneous chemical etching, ion preferential sputtering, incident species reflexion, passivation layer formation and redeposition. Kinetic parameters are introduced as input data obtained by experimental measurements. The etched substrate is discretized by a series of uniform square cells which size defines a real number of silicon atoms. Local surface displacement is modelled by "full" cells dis/re-appearance when an etching or redeposition process occurs. This microscopic method gives an instantaneous picture of surface state during the process. In particular, it permits to follow the F/Si and O/Si surface coverage on the sidewalls versus depth and time. These information are useful to understand the transport of species in the trench. The model shows that undercut and bowing development depends on kinetic surface parameters.

PS-TuP22 Ion Trajectories in Electron-shading Damage, ***T.G. Madziwa***, *F.F. Chen, D. Arnush*, University of California, Los Angeles

In electron-shading damage, the photoresist is charged negatively, preventing electrons from entering the trench, while ions are accelerated toward the bottom of the trench. We have numerically calculated the effect of these fields on the ion trajectories. The ions are injected at acoustic speed from a sheath edge far from the substrate, and the electrons have a Maxwell-Boltzmann distribution. The photoresist and trench walls are assumed to be insulators, and the trench bottom a conductor at various potentials relative to the sheath edge. The potentials on all surfaces are given initial values, and a Poisson solver is used to compute the electric field everywhere. The ions' trajectories in this field are then computed. Setting the flux of ions to each dielectric surface equal to the Maxwellian electron flux yields a new value of the surface charge. The E-fields and trajectories are then recomputed, and the process iterated until the values converge. It is found that the E-field is concentrated near the entrance to the trench, the only place where the charges matter. The ions receive a kick there and then coast the rest of the way. Thus the trajectories are very sensitive to the exact shape of the photoresist and will change as the etch progresses.

PS-TuP23 LIF Measurement of Catalytic Species in Plasma Plume for Carbon Nanotubes Formation by PLA, ***T. Ikegami***, *M. Uchiyama, K. Ebihara*, Kumamoto University, Japan, *J. Asmussen*, Michigan State University

Single wall carbon nanotubes (SWNT) have been synthesized in an inert gas, 500 Torr, atmosphere by using pulsed laser ablation (PLA) on a graphite target containing metal catalysts such as Fe, Ni/Co. In order to clarify the mechanism of formation of carbon clusters and to understand the role of catalytic atoms in the formation of SWNT, carefully diagnostic experiments have been conducted. Specifically a carbon and Fe or Ni composite target was ablated by KrF excimer laser or YAG laser in Ar gas environment of several hundred Torr. Carbon species such as atoms, ions and molecules C_2 and C_3 in the ablation plasma plume were measured using absorption spectroscopy, ion probe, laser induced fluorescence (LIF) method, respectively. At the same time density profiles of catalytic Fe and Ni atoms were also measured using LIF method. By changing laser fluence on the target and laser wavelength (λ=248nm, 532nm, 1064nm), the relationship between carbon species and catalytic species profiles was investigated. Also the effect of magnetic and electric fields on these species was examined. Nanoparticulate soot was collected and refined to obtain nanotubes after the ablation. Properties of nanotubes were measured using AFM, XRD, FT-IR, XPS and ESR. Preliminary measurements on carbon species indicate that their density and profiles are strongly affected by laser wavelength and fluence. Species concentrations vs. the type of the catalyst will be also discussed. This research is partly supported financially by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (C), Japan.

PS-TuP24 Surface Investigation of Bone Tissue Treated with Non-thermal Plasmas, ***J.-C. Cigal***, *C.Y.M. Maurice, E. Wagenaars, L.J. van Ijzendoorn, A.H.F.M. Baede, R. Huiskes, G.M.W. Kroesen*, Eindhoven University of Technology, The Netherlands

In the last few years, much effort has been carried on the development of biocompatible plasma. Such technique directly derived from material surface processing could lead, in a long term, to a plasma-based cure for disease like restenosis, bone cancer, osteoporosis, or eczema. Our group recently developed a non-thermal plasma needle working at atmospheric pressure for this purpose. In order to be able to investigate the interaction between the plasma and living tissue, we used a low pressure plasma operating on a larger area. Because of its stability, bone tissue appeared to be the most suitable bio surface for this study. It is composed of a mineral network constituted of Calcium-hydroxy-apatite, combined with organic material (e.g. collagen). The samples have been exposed to an inductively coupled plasma, using different gases (Argon, Krypton, Helium, and Oxygen in mixture). The samples have been analysed by using infrared spectroscopic ellipsometry before and after treatment. This technique based on Fourier transform analysis presents the advantage of giving accurate information on the chemical composition of the surface of the tissue. Results have been compared with other techniques such as EDX, environmental scanning electron microscopy (ESEM), and nano-indentation. We also performed some ion beam diagnostics like RBS, PIXE, ERDA, and nuclear reaction analysis. These complementary experiments allowed us to determine the elemental of the bone tissue. These parameters are strongly connected to the above mentioned diseases.

PS-TuP25 Surface Modification of Polymers in the Development of Anti-Microbial Coatings for Medical Devices, ***G.Sh. Malkov***, *E.R. Fisher*, Colorado State University

The applying of polymers in medical devices requires strict control over material surface chemistry. Plasma-Enhanced Chemical Vapor Deposition (PE-CVD) of fluorinated monomers is a useful technique for altering the surface chemistry without affecting bulk properties and obtaining low energy surfaces. Plasma-deposited fluoropolymers demonstrate chemical inertness, lubricity, and blood compatibility. In this study, we have investigated the surface modification and characterization of polystyrene and polyvinyl chloride. Chemistry and wettability differences of modification steps were characterized using angle-resolved X-ray photoelectron spectroscopy (XPS) and static contact angle measurements. Polymer surfaces have been coated by the thin film deposition using a capacitively coupled pulsed plasma RF-discharge system with C_2F_8 and C_4F_8 as precursors. Resulting fluorocarbon films display a high hydrophobicity (water contact angle ~110°). Then the samples were activated by RF-plasma glow discharge in the presence of argon gas and

coated with Pluronic F108, which is inert to cell adhesion. The water contact angles decreased to approximately 60°. Differences in the ability to modify the fluoropolymers, depending on both monomers and plasma polymerization conditions, are observed. The composition of the surfaces will be presented as well as data from ageing studies. Preliminary XPS and contact angle measurements show a change in composition of the surfaces on time. Data from protein adhesion studies using fluorescently tagged proteins will also be presented.

PS-TuP26 Optimization of Four-component Gas He-Ne-Xe-Kr for High Efficiency Plasma Display Panel, ***T.W. Kim***, *S.U. Kwon, H.J. Hwang*, Chung-Ang University, Korea

Plasma display panel (PDP) has been spotlighted as one of the promising candidates for a flat panel display. The improvement of luminous efficiency is one of the most important issues in making a plasma display into a large flat panel device. The most fundamental element determining the discharge property is the discharging gas injected into the cell of AC PDP. Therefore, we aimed to find the optimum gas composition for maximum electric discharge. A new composition of a four-component gas, He-Ne-Xe-Kr, is proposed in order to achieve a high luminous efficiency (maximum electric discharge) in color PDP. The model utilized here is based on self-consistent simulation of the microdischarges in the PDP cell. The space and time variation of the electric field within the cell is self-consistently determined by solving the fluid equations for ions and electrons together with Poisson's equation, subject to the boundary conditions imposed by the electrode boundaries. The electrical model is coupled to a model of excited species kinetics. The density of $Xe^*(^3P_1)$ and electron, which is critical in determining the luminous efficiency, were calculated using the two-dimensional model. and The efficiency of the electrons in exciting UV emitting states of Xe was calculated. The results were then compared with measurements of luminous efficiency to identify the optimum mixing condition of He(70): Ne(27): Xe(3)-Kr gas for a color PDP.

PS-TuP27 Bond Strength Improvement of Plasma Sprayed Hydroxyapateite/Titanium Composite Coatings on Titanium: Partial Nitriding of Titanium Deposits by RF Thermal Plasma, ***M. Inagaki***, *Y. Yokogawa, T. Kameyama*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Plasma sprayed hydroxyapatite (HA) coating on titanium alloy substrates has been used for medical application to promote the osteoconductivity of implanted materials. For practical application, such as artificial joint, HA coatings with excellent adhesion to the substrate have been strongly demanded to ensure long-time fixation. However, due to the large difference in thermal expansion coefficients between coated ceramics and metal substrates, residual stress arises at the metal/ceramics interface. Such residual stress often causes cracks and reduces the bond strength of coatings. Recently, we have developed a radio frequency (RF)-TPS method that allows us to obtain strong adhesion between HA coatings and titanium (Ti) substrates by employing a HA/Ti composite coating. Here, we briefly describe a promising method to improve the adhesiveness of HA/Ti composite coatings by RF-TPS method. HA/Ti composite coatings were deposited on titanium substrates by a RF-TPS method with RF input powers of 10-30 kW. Partial nitriding of Ti deposits conducted by plasma-enhanced reaction during plasma spraying of HA/Ti composite coatings. The ratio of HA and Ti powders supplied into the plasma was precisely controlled by two microfeeders so as to change the composition from Ti-rich to HA-rich toward the upper layer of the coatings. The bond (tensile) strength of HA/Ti composite coatings was 40-65 MPa. XRD patterns of Ti coatings without HA showed that titanium nitride was formed at the surface of titanium deposits sprayed with N_2 plasma gas. Scanning electron microscopic observation showed an acicular texture on the Ti deposits prepared with N_2 added plasma gas.

PS-TuP28 Reactive Sputtering in Hollow Cathodes, ***S.I. Shah***, *A. Pradhan*, University of Delaware, *S. Berg, T. Nyberg*, Uppsala University, Sweden

Hollow cathode sputtering, due to the enclosed geometry, presents a unique opportunities that can be favorably utilized for depositing conformal coatings on complex substrates. Additional advantages related to reactive sputtering can be obtained from such enclosed sources. We have characterized a Hollow Cathode Source (HCS) for reactive sputtering from metal targets. Deposition rates close to that of metals are obtained during reactive deposition of oxides. We will present TRIM modeling to show the effect of oblique emission of the sputtered flux on the total sputtering rate. Similar effects can be seen from reflected neutrals. No hysteresis behavior in any of the sputtering parameters, typical for reactive sputtering in planar sputtering, was observed. We will present a model which will include the consideration of the relative cathode to anode areas, redeposition of the sputtered flux, pumping speed, relative flux of the metal and the reactive gas, etc., for hollow cathodes. The model shows that reactive sputtering in a circular confined geometry can be carried out at a very high deposition rate without the complexity of a hysteresis in the sputtering parameters.

PS-TuP29 Process-Induced Damage by the Low Angle Forward Reflected Neutral Beam Etching, ***D.H. Lee***, *M.J. Chung, H.K. Hwang, G.Y. Yeom*, Sungkyunkwan University, Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particles such as positive ions and photons generated in the plasma which causes radiation damage causing 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 the previous study, a neutral beam was formed using a low angle forward reflected neutral beam technique as a possible anisotropic etching technique without charging and its degree of neutralization and etch characteristics were investigated. When the ion beam was reflected at a reflector at the angles lower than 15 degrees, most of the ions reflected were neutralized and the lower reflector angle showed the higher degree of neutralization. In this study, process-induced damages during the etching of SiO_2 were investigated in addition to the etch rates and the etch properties of SiO_2 for fluorine-based gases using the low angle forward reflected neutral beam etching system. Surface contamination was performed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Also, possible neutral beam induced charge damage was examined through electrical characteristics such as C-V, I-V, and breakdown voltage of the gate oxide and the Si-SiO_2 interface after the etching.

PS-TuP30 Experimental Study on New Sterilization Process by using Plasma Source Ion Implantation Method with N_2 Gas, *M. Yoshida*, Mitsubishi Heavy Industries, Ltd., Japan, ***T. Tanaka***, *S. Watanabe, T. Takagi*, Hiroshima Institute of Technology, Japan, *M. Shinohara*, Kurita Seisakusho Manufacturing Co., Ltd., Japan, *S. Fujii*, Adtec Plasma Technology Co., Ltd., Japan

Plasma source ion implantation (PSII) with negative high voltage pulses has been applied to uniform sterilization process for three-dimension shaped species. This process was performed with and without external plasma source, that has been generated by inductively coupled antenna using 222 kHz RF voltage. The pulsed high negative voltage (~10 μs pulse width, 300~900 pulses/sec, 9~16 kV) was applied to the electrode in this process at the gas pressure of 2~7 Pa of N_2. This process has been found out to be capable of generating glow discharge plasma around SUS electrode, on which quartz glass plate with biological materials are placed. We have obtained a preliminary result that the PSII process has reduced log numbers of Bacillus Pumilus with N2 gas plasma generated by pulsed RF and DC voltages. This experimental result is showing a 5~6 $\log_{10}$ colony forming units reduction in Bacillus Pumilus with dried culture media by 5~10 minutes exposure. The effect of several discharge conditions such as gas pressure, pulse voltage, and RF power have been investigated experimentally. The RF discharge without negative high voltage pulses has been found to reduce colony forming units by ~3 $\log_{10}$ for 40 minutes exposure as well. However, negative high voltage pulses are necessary to achieve 5~6 $\log_{10}$ reduction of Bacillus Pumilus for ~5 minutes exposure. The state of Bacillus Pumilus on quartz glass was observed by scanning electron microscopy (SEM) with and without exposure, which is showing the surface of Bacillus Pumilus has some damage by the plasma treatment, and no damages are seen in Bacillus Pumilus by just setting in vacuum. From these experimental results, some possible effective options for the plasma sterilization systems are discussed, such as H_2O vapor mixture to generate dense OH radicals, Ar or He gas usage, and electron bombardment by the positive high voltage pulses.

PS-TuP31 Study on the Characteristics of Neutral Species in the Low Angle Forward Reflected Neutral Beam Etching System, ***M.J. Chung***, *D.H. Lee, N.G. Cho, G.Y. Yeom*, Sungkyunkwan University, Korea

submicron semiconductor devices as well as future nanoscale devices. To avoid the charge-related damage, several low-damage processes have been proposed and one of the techniques to avoid the problem is to use neutral beam etching. One of the techniques fabricating a neutral beam is to use a low angle reflection of the ion beam where ions extracted from the ion source are neutralized by a low angle reflection during the reflection. Previous study showed that, by the reflection of the ion beam at 5 degree angle of incidence, most all of the ions could be neutralized. The degree of neutralization was similar to the all of the gases used in the experiment such as SF_6, NF_3 and CF_4 which can be used for the etching of SiO_2 and Si. Also, using radical beams from these gases, nearly vertical SiO_2 etching could be obtained. Even though the ions reflected at the reflector were proven to be

neutralized, the energy distribution of these reflected neutrals and the possibility of cracking after reflection for reactive gases such as SF_6, NF_3, and CF_4 need to be investigated. In this study, energy and species of neutrals generated by the low angle forward reflection of reactive ions were analyzed by means of direct sampling using a quadrupole mass spectrometer (QMS) with double ion energy analyzers modified to detect neutral energy and species. Using this modified mass spectrometer, the concentration and energy distribution of each neutral species were investigated as a function of rf power, gas flow rate, and acceleration/extraction voltage of the ion gun for various reactive gases. The correlation of the etch characteristics of SiO_2 and Si with the characteristics of the measured incident neutral species were investigated to study the etch mechanism of Si and SiO_2 using the low angle reflection technique.

PS-TuP32 Improvement of Luminance and Luminous Efficiency through the Optimum Gas in AC Plasma Display Panel, ***S.J. Lee***, *H.-J. Hwang*, Chung-Ang University, Korea

The luminance and luminous efficiency improvement is a key issue for making a plasma display into a large flat panel device. We suggest a new combination of the mixture gas, in order to find the optimum mixture gas in plasma display panel. The influences of Ar, Kr addition to Ne{96%}-Xe{4%} and He{70%}-Ne{27%}-Xe{3%} mixture gases are experimentally investigated for surface discharge of alternating current plasma display panel. When rare Ar { 0.01% - 0.1% }, Kr { 0.01% - 0.1% } are added Ne-Xe and He-Ne-Xe mixture gases, the luminance increases over 20% and luminous efficiency increases over 25% at 200Torr. It is sure that luminance and efficiency are effected by penning electrons. Also, this influence of Penning effect is shown by increased wall charge { 15% - 25% } which is experimentally measured in plasma display panel.

PS-TuP33 Surface Cleaning of Organic Materials on Metal by Atmospheric Pressure Plasma, ***C.H. Yi***, *Y.H. Lee*, SungKyunKwan University, Korea, *E.S. Choi*, LG-PRC, *H.C. Woo*, Korea Vacuum Tech., *G.Y. Yeom*, SungKyunKwan University, Korea

Due to the various advantages of the use of atmospheric pressure, recent studies on the surface cleaning of organic materials are concentrated on the atmospheric pressure plasmas instead of low pressure plasmas. In this study, atmospheric pressure plasmas were generated using a capillary dielectric covered electrode and AC power supply(3-15kV) of low frequency to clean organic materials on metal surfaces such as Ag and Cu and the effects of process conditions and cleaning gases on the cleaning properties have been investigated. As the cleaning gases, He and O_2 were used as the ignition gas and cleaning gas, respectively. In addition to these gases, N_2, Ar, and SF_6 were added to improve the effect of surface treatment. The small addition of O_2 to He increased the surface cleaning rate due to the increase of oxygen radicals in the plasmas, however, the further addition of oxygen decreased the surface cleaning rate possibly due to the decrease of plasma density by the formation of oxygen negative ions between oxygen molecules and electrons in the plasma. The additional mixture of N_2 to O_2/He further increased the surface cleaning possibly due to the increased chemical reaction with surface contaminants resulting in the increased volatilization and removal from the surface. Surface characteristics after the plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS) and showed the decrease of carbon contaminants on the metal surface by the atmospheric pressure plasma treatment. Decrease of contact angles of water on the plasma cleaned surface was also observed.

PS-TuP34 A New Design in Atmospheric Plasma Generation Improves Versatility for Surface Treatment Applications in Industry, ***D. Chrysostomou***, *S. Goloviatinskii*, TePla AG, Germany

Inexpensive materials, with excellent applied bulk properties, often require surface modification to improve bondability and printability. Plasma treatment is an established industrial method for such surface modifications. Use of atmospheric plasma is more cost effective than low pressure systems and can be easily operated in continuous mode. This presentation introduces a novel design in atmospheric plasma generators that overcomes many of the disadvantages previously associated with this treatment method. A low current , 100 - 250 mA, high voltage, 1000 - 1700 V, pulsed DC arc discharge generator permits electrode construction with small dimensions. The light weight of each electrode assembly, 200 g, allows low cost operation by robotic systems. Fast point-to-point processing is possible due to very short plasma ignition times. The electrode design confines current and voltage within the discharge chamber and ensures no electrical charge transfer to the treatment surface (critical for metals and metal/dielectric hybrids in wire bond applications). Very high density equilibrium plasma, 100 W/cm^3, ensures uniform and highly effective treatments at high speed, up to 2m/sec for polycarbonate, acrylic, and silicone materials. The electrode construction produces a low temperature discharge without generating UV or ozone. NO_x levels are in the order of 100 ppm and are managed by standard filter systems. XPS analysis shows no contamination of sputtered electrode material, an essential requirement for medical, optical, and IC applications. Treatment widths of up to 40 mm are possible with a single power supply, and these systems can be further arrayed for extended treatment widths. Current electrode lifetimes exceed 1500 hours.

Plasma Science
Room: C-103 - Session PS+NT-WeM

Plasma Science and Technology for Nanostructures
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

8:20am **PS+NT-WeM1 Plasma Enhanced Chemical Vapor Deposition of a Dense SiO_2 Cap Layer on Low-k Nanostructured Porous Silica**, ***Y.B. Jiang***, *N. Liu, C.J. Brinker, J.L. Cecchi*, University of New Mexico

Surfactant-templated self-assembled nanostructured porous silica is a promising material for low-k interlevel dielectrics (ILDs) in integrated circuits. With mono-dispersed pore sizes as small as 2 nm and an ordered pore structure, nanoporous silica has excellent mechanical and thermal properties, even at porosities high enough for k values of 2 and below. For ILD applications, the pores must be capped to prevent adsorption on pore surfaces during subsequent processing, such as the deposition of a copper diffusion barrier. In this work, we report on a process for capping nanoporous silica with a dense-but-thin SiO_2 layer that acts as a diffusion barrier without significantly increasing the overall dielectric constant of the ILD. Nanoporous silica was deposited on a silicon wafer by spin coating with a sol-gel solution. After spin coating, the films were solidified by heating. The pore surfaces were rendered hydrophobic by soaking the films in a 6% HMDS solution, which terminated the pore surfaces with methyl groups. An SiO_2 cap layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) in an inductively-coupled plasma reactor, using a SiH_4/O_2/Ar gas feed mixture. RF power, total pressure, gas composition, and flow rate were varied systematically to produce a high-density film with low surface roughness. The corresponding deposition rate resulted in 50 nm-thick films in approximately 15 minutes. N_2 absorption measurements performed with a surface acoustic wave (SAW) technique indicate a reduction of more 10 between the capped and the uncapped nanoporous film. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements both confirm that the pore structure in the nanoporous silica is unchanged by the capping process. Fourier transform infrared (FTIR) detection of methyl groups shows that the hydrophobicity of the nanoporous silica remains after the dense SiO_2 cap layer is deposited.

8:40am **PS+NT-WeM2 RIE processes of Formation of Nanometer-Scale Dot Arrays**, ***Y. Zhang***, *K.W. Guarini, E. Sikorski, C.T. Black, T.J. Dalton*, IBM T.J. Watson Research Center

Nanometer scale structures are increasingly merging into microelectronics and other applications. One of the challenges of fabricating nanometer scale structures is the simultaneous scaling of vertical and horizontal features. As the horizontal feature scale shrinks down to nanometer sizes, the vertical scale often shrinks at a faster rate. When using these materials for masking layers, this leads to new challenges in fabricating multi-layer nanometer scale structures for a variety of microelectronics applications. In this paper, we explore the challenges of plasma RIE processing to fabricate densely-spaced, uniformly-sized nanometer-scale dot arrays over large wafer areas based on self-organizing diblock copolymers. High selectivties among variety materials, precise CD control, real time process monitoring, and flexible and uniform plasma processing conditions are necessary for fabricating nano-scale structures with high aspect ratios (AR), e.g., ~ 20nm polysilicon hole or column arrays with AR > 15:1. The results show the versatility of RIE process techniques through examples of dot arrays formed of conducting, insulating, and polymeric materials. These fabrication processes vary in complexity, utility, and degree of optimization, and we discuss the relative merits of each. The ability to create uniform nanoscale features below lithographic resolution limits may enable key applications in fields such as magnetic recording and microelectronics.

9:00am **PS+NT-WeM3 Efficient Production of Single-Wall Carbon Nanotubes by Means of the Gravity-free Gas Arc Dischargee**, ***T. Mieno***, Shizuoka University, Japan, *M. Kanai*, University of London, UK, *H. Shinohara*, Nagoya University, Japan **INVITED**

Single-wall carbon-nanotube (SWNT) are attracting much attention by their unique structures and properties, and applications of nanotubes are demonstrated as a cold electron emitter, strong wire, electronic devices and hydrogen absorber. The SWNT are produced by the gas-arc method as same as the fullerene production method. A carbon anode mixed with metal catalyst is arc sublimated in He gas (p> 40 kPa), and high density carbon particles deposit on metal particles in hot gas atmosphere making nano-pipe structures, diameter of which is about 1 nm. As these nanotubes, metal particles and another carbon clusters are flown up by the heat convection, the reaction time is limited by this heat convection. If the heat convection is suppressed by the gravity-free condition, diffusion speed of these particles is suppressed and longer reaction time can be expected.[1] In order to examine this gravity effect, the 12m-high vertical swing tower[1] is used and the carbon nanotubes are produced in the gravity-free condition.[2] Integrated gravity-free sublimation time is about 14 min. After the discharge, the carbon soot is collected and its weight is measured. As a result, production rate of the carbon soot including SWNT about 7 times increase in the gravity-free condition compared with that of the normal gravity condition. By the TEM (microscope method) their morphology is observed and more (about 2 times) dense bundle of SWNT is confirmed in the gravity-free condition. Thickness of the produced nanotube is measured by the Raman scattering method, and fatter nanotube (mainly d= 1.4 nm) is produced in the gravity-free condition compared with the normal-gravity case.

[1] T. Mieno, Jpn. J. Appl. Phys. 37 (1998) L761.
[2] M. Kanai, T. Mieno, H. Shinohara et al, Appl. Phys. Lett. 79 (2001) 2967.

9:40am **PS+NT-WeM5 Patterned Growth of Vertically Aligned Carbon Nanofibers using a High Density Plasma Enhanced Chemical Vapor Deposition Process**, ***J.B.O. Caughman***, *L.R. Baylor, M.A. Guillorn, V.I. Merkulov, D.H. Lowndes*, Oak Ridge National Laboratory

Patterned arrays of vertically aligned carbon nanofibers (VACNFs) have been grown using a high density plasma enhanced chemical vapor deposition process. The nanofibers are grown from a nickel catalyst that can be patterned to form arrays of individual isolated electron emitters. Forests of nanofibers, as well as single isolated nanofibers have been grown. An inductively coupled plasma source is used to grow the fibers. The plasma source operates at 13.56 MHz and couples power via a flat spiral coil. The plasma is composed of hydrogen and either acetylene or methane. The VACNFs are grown on a heated substrate located downstream from the ionization zone. Typical growth temperature is 700 degrees C. The energy of the ions impacting the growth surface is controlled by radio frequency bias, with typical self-bias voltages of between -50 and -300 volts. Plasma conditions are related to growth results by comparing optical emission from the plasma to the physical structure and electron emission from the nanofibers. For example, as the acetylene flow increases, the optical emission from the plasma indicates a decrease in atomic hydrogen production and an increase in molecular carbon production. The decrease in atomic hydrogen production results in a decrease in the chemical etching component during nanofiber growth. Plasmas that contain a high hydrogen to carbon ratio result in fairly narrow nanofibers, while plasmas with a high carbon to hydrogen ratio result in nanofibers with a broader base with more of a cone-like structure. The threshold electric field from isolated emitters has been measured and is typically 30-50 volts/micron and can vary with growth conditions. The relationship between plasma conditions and growth results/performance will be presented.[1]

[1]Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

10:00am **PS+NT-WeM6 Carbon Nanotubes by ICP-CVD: Growth, Characterization, Plasma Diagnostics, and Modeling**, ***D.B. Hash***, *L. Delzeit, K. Matthews*, NASA Ames Research Center, *B.A. Cruden*, Eloret Corporation, *M. Meyyappan*, NASA Ames Research Center

Applications in field emitter devices, electrode and sensor development require a very high degree of vertical orientation of carbon nanotubes (CNTs) on the substrate. This is not possible using thermal CVD. The inherent electric field in a direction normal to the substrate in a plasma process enables achievement of vertical orientation of the nanotubes. We have built an ICP reactor and grown multiwalled carbon nanotubes (MWNTs) from hydrocarbon feedstock (CH_4, C_2H_2, and C_2H_4) diluted with hydrogen. The MWNTs have been characterized using SEM, HRTEM, and Raman scattering. The MWNTs are highly aligned and suitable for the applications mentioned above. Results as a function of pressure, substrate power, and temperature will be discussed. To understand the effects of process parameters on growth as well as mechanisms - including identification of species responsible for nanotube growth, we have undertaken a 2-D plasma modeling of the process. Modeling results are compared with plasma diagnostics using optical emission spectroscopy, UV Absorption, and Residual Gas Analysis (RGA).

10:20am **PS+NT-WeM7 Zinc Oxide Nanowires Grown by Plasma Assisted Chemical Vapor Deposition**, ***J.B. Baxter***, *E.S. Aydil*, University of California, Santa Barbara

Zinc Oxide is a wide band gap semiconductor (Eg=3.37eV) that can exhibit visible and UV luminescence, piezoelectricity, and high conductivity. ZnO nanowires and hexagonal columns have been grown using plasma assisted chemical vapor deposition, using either metallic zinc or metalorganic

precursors. Nanowire growth is catalyzed by monodisperse gold nanoparticles (20 nm diameter) dispersed on a substrate from a colloidal solution. Transmission electron microscopy and electron diffraction show that single crystal ZnO nanowires grow from the gold particles in the <0001> direction. The nanowires have monodisperse diameters determined by the diameter of the gold particles (~ 20nm), and can grow to several microns in length. Energy dispersive x-ray spectroscopy confirms that the wires have a Zn:O ratio of 1:1. ZnO columns were formed by subliming metallic zinc in oxygen plasma, with the columns growing in the <0001> direction from the zinc surface. The columns are several 100 nm in diameter and are hexagonally faceted. Cathodoluminescence results show that both wires and columns emit photons upon excitation by electrons, with the columns emitting most light through the top face. This suggests that ZnO nanowires act as light pipes by internally reflecting the emitted light, making them good candidates for UV lasing. Because the gold particles from which the wires grow can be closely packed, the wires can be grown on a substrate in very dense, high surface area arrays. This property suggests that ZnO nanowires are also ideally suited toward application as the mesoporous semiconductor in dye sensitized (Gratzel) solar cells.

Plasma Science
Room: C-105 - Session PS-WeM

Conductor Etch II
Moderator: S.J. Ullal, Lam Research Corporation

8:20am **PS-WeM1 Plasma Etch Chemistries for III-V Lasers and Light-Emitting Diodes**, ***S.J. Pearton***, University of Florida **INVITED**

A review will be given of plasma chemistries for etching AlGaN/InGaN, InP/InGaAsP and AlGaAs/GaAs diode lasers and light-emitting diodes. With Cl_2-based chemistires, it is generally necessary to heat the sample when etching In-containing compounds, because of the low volatility of $InCl_x$. By contrast, the use of Br_2 or I_2 based chemistries produces practical etch rates at room temperature. Plasma-induced damage can play a significant role in determining device performance through effects on ohmic contact resistances or optical output power. Special attention must be paid to the quality of the initial lithography for patterning resist, since sidewall roughness is transferred into the semiconductor during subsequent etching. Gratings for DBR or DFB layers are also readily created using holographic lithography and plasma etching.

9:00am **PS-WeM3 Surface Chemical Changes of Aluminum During NF3-Based In-Situ Chamber Cleaning: Critical Discharge Parameters**, ***X. Li***, *G.S. Oehrlein, X. Hua, L. Ling*, University of Maryland, *E. Karwacki, B. Ji*, Air Products

During plasma-based in-situ chamber cleaning of deposited dielectric films using NF3, a significant transformation of aluminum into AlF3 can occur. We studied the roles of fluorine atoms and ion bombardment in this process by employing NF3 discharges mixed with He, Ne or Ar. Polished Al 6061 alloy coupons and sputter-deposited Al films were used. Typical process conditions were a pressure of 1 Torr, a total flow rate of 300 sccm, and power levels up to 300 W RF bias power for a 125 mm diam wafer. Aluminum erosion rates and surface chemistry changes, and information on the species that evolve from the surfaces during the process were obtained by real-time ellipsometry and mass spectrometry, respectively. X-ray photoemission spectroscopy characterization of processed Al surfaces was also performed. We find that a complex Al-fluoride layer is produced by the plasma processes. For RF-based discharges employing NF3 a threshold RF power exists below which a thicker reacted Al-fluoride layer is not produced (about 2 W/cm2 for our reactor). When Al is exposed to an NF3 RF discharge above this power level, a thick reacted Al fluoride layer is produced. If instead a He/NF3 discharge is used, the Al surface modifications are minimized at high RF power as long as the NF3 concentration is less than 40%, and an increasingly thicker Al fluoride layer is produced with a greater proportion of NF3 in He/NF3. In addition, we will report RF electrical characterization of NF3/He discharges under these processing conditions, and results of comparative studies using Ne/NF3 and Ar/NF3 discharges, and microwave remote plasma production.

9:20am **PS-WeM4 Metal Etching in High-Density Plasmas**, ***R. Blumenthal***, *A.S. Orland*, Auburn University

Metals are found at the heart of many important current and developing device technologies, such as GMR read heads, MRAM and FeRAM. As the scale of these devices continues to be reduced, high performance etch technologies will become a necessary component of the fabrication of these devices. The chemical mechanisms of high-density plasma etching of Fe, Ni, Co and their alloys will be presented for a range of etch chemistries ranging from the more traditional etching of the metals with Cl_2 to the more novel example of $CO-NH_3$ etching and finally to a new etch chemistry based on H_2-CO gas mixtures. The chemical mechanisms of etching have been determined from measurements of the variation of chemical composition as a function of plasma conditions, using supersonic pulse, plasma sampling mass spectrometry.

9:40am **PS-WeM5 Effects of Dry Etch Process for Platinum Upper Electrodes on Electrical Properties of High-k (Ba,Sr)TiO_3 Thin-Film Capacitors**, ***D.-S. Wuu***, *R.-H. Horng, C.-Y. Kung*, National Chung Hsing University, Taiwan ROC

Inductively-coupled-plasma (ICP) etching behavior of the platinum (Pt) thin films has been characterized with Ar gas by varying the etching parameters such as chamber pressure, ICP power, and bottom rf power. After the dry etch process, the restoring method of plasma-induced damage was investigated in terms of rapid-thermal and furnace annealing. Quantitative analysis of the etch damage was attempted to discuss the mechanism of leakage current density and dielectric constant with various bottom rf power and ICP power in Pt/(Bs,Sr)TiO_3(BST)/Pt capacitor. It was found that the parameters of etching process for the top electrodes of BST capacitors would influence the methods of recovering technique. In this study, a better condition with lower leakage current density was observed under a coil power of 1000 W, bottom rf power of 100 W, and chamber pressure of 0.67 Pa. The plasma-induced damage samples can be effectively recovered with furnace annealed at around 600°C in oxygen ambience. It can not only improve the leakage current density less than $5x10^{-8}$ A/cm^2 under an applied voltage of 1 V, but also enhances the dielectric constants to 350 for the damaged samples.

10:00am **PS-WeM6 Residual-Free Reactive Ion Etching of the Bell Contact Ti/Pt/Au**, ***G.F. Franz***, *R. Kachel, S. Sotier*, University of Applied Sciences, Germany

The etching of the complete Bell contact consisting of a layer of Ti/Pt/Au was performed in highly reactive plasmas containing Cl_2 for Ti, $PF3_3/NF_3$ for Pt, and Cl_2 and/or BCl_3 for Au. All the constituents of the Bell contact form volatile compounds in either capacitively-coupled low-density plasmas or high-density plasmas generated by electron cyclotron resonance. This is a conditio sine qua non for surfaces and sidewalls which have to remain free of any residues. Its functionality was demonstrated as self-adjusting mask for a surface-emitting laser.

10:20am **PS-WeM7 Advanced Metal Gate Etch with 193nm Lithography in a Silicon Decoupled Plasma Source Etcher (DPSII)**, ***D. Yan***, *M. Shen, D. Shashank*, Applied Materials, *T. Chowdhury, C. Yang*, Cypress Semiconductor

193nm lithography is becoming increasingly important as the critical dimensions of semiconductor devices continue to scale down towards sub-0.10um. From dry etching perspective, however, 193nm resist brings new challenges due to its poorer plasma etch resistance, line edge roughness and lower thickness compared to 248nm DUV resist. Consequently, issues such as line edge roughness and poor profile control were observed after dry etch processing using etch processes developed for 248nm resist. This paper presents a successful development of advanced 0.1mm metal gate application using 193nm lithography on Applied Materialsâ€™ decoupled plasma etcher (DPSII). The integrated process involves a hard mask open with ex-situ resist strip followed by metal/poly dual gate etching. Process chemistry and process parameters for nitride mask step were thoroughly investigated. With CF4/CHF3 based chemistry, the process achieved high nitride to resist selectivity with straight nitride profile and smooth sidewall. Less than 7nm 3-sigma of CD bias uniformity was obtained across the wafer with edge exclusion up to 4mm on a 200mm substrate. Process parameters such as pressure, gas ratio and the total fluorine-containing flow were shown to be the most influential on resist selectivity, profile and CD control. A careful balance of these parameters needs to be maintained in order to deliver an overall process. The subsequent W/WN/poly gate etch features a three-step approach that has produced straight profiles, excellent CD control and excellent gate oxide integrity. Post-etch measurement of line edge roughness shows comparable performance to that obtained on 248nm resist. Bright field ultra sensitive defect monitoring on product wafers showed comparable performance to previous 248nm resist poly gate process. Process trends and proposed mechanisms are addressed in detail in the paper.

10:40am **PS-WeM8 Effect of Carbon Based Polymer Formation on Process Stability in Polysilicon Etching**, *S. Xu, S. Deshmukh*, ***Th. Lill***, Applied Materials, *O. Joubert*, CNRS/LTM, France

High density plasma at low pressure has been used extensively in etching ultra-small feature devices to achieve precise critical-dimension control. In

such a processing environment, plasma properties become significantly dependent on the wall condition of the reactor through plasma wall interactions. Commonly, halogen containing silicon oxides are deposited on the chamber walls during polysilicon etching. Recently, in-situ dielectric mask open or dielectric anti-reflective coating open steps are being used more frequently. These steps generate carbon based deposits on the chamber walls. Another source of carbon polymers are CF4 and other CxHyFz additives used in silicon etching to achieves good n/p etch behavior and dense/iso microloading. This paper extends previously published studies on the influence of polymer formation on the chamber walls to carbon based polymers. The effect of surface polymerization has been characterized by studying the variation of the plasma properties and process performance. Clean, oxide covered and carbon covered chamber wall are being compared in terms radical densities, plasma emission properties, etch rates, and critical gate dimensions. Effective approaches to reduce the impact of chamber wall on the plasma and process stability will be discussed.

Plasma Science
Room: Exhibit Hall B2 - Session PS+TF-WeP

Plasma Etching & Deposition

PS+TF-WeP1 Expanding Thermal Plasma Deposition of UV Filters and Abrasion Resistant Coatings, ***C.D. Iacovangelo***, *M. Schaepkens*, General Electric Global Research Center

Use of plastics in large area applications such as automotive glazing require deposition of abrasion resistant and inorganic UV filter coatings for protection. These coatings must be hydrolytically stable and weather able. We have developed expanding thermal plasma (ETP) deposition processes for high rate, large area deposition of ZnO and doped-ZnO UV filters and organo-silicon based inter-layers and abrasion resistant layers on polycarbonate (PC) substrates. This paper will describe the ETP processes used to deposit these materials and the effect of processing parameters on the deposition rate, UV absorbency, hydrolytic stability and weather ability of these materials and multi-layer packages. ZnO was deposited from diethylzinc, dimethlyzinc, and by thermal evaporation of metallic Zn into the ETP Ar/Ox jet. Abrasion resistant coatings and inter-layers were formed from TMDSO, HMDSO, and D4. Using these processes, highly stable, weather able coatings at deposition rates of 20 microns/minute on PC substrates were obtained. Processing parameters, degree of doping, and precursor selection were critical to achieving ZnO with high UV absorbency and hydrolytic stability. ZnO coatings of 0.5 microns thick provided UV absorbency at 350 nm of 4.0. ZnO coatings from metallic zinc were crystalline and resulted in superior stability to deposits from either diethyl or dimethylzinc. Highly abrasion resistant coatings, Taber abrasion of 2 at 1000 cycles, were obtained with all of the organo-silicone materials examined, however, UV absorbency of the coatings limit the practical application of all but D4. Equivalent 10-year life of multi-layer packages has been demonstrated in accelerated weathering tests.

PS+TF-WeP2 Tuning the Material and Electrical Characteristics of ZrO_2 Film Obtained by Plasma Enhanced Chemical Vapor Deposition, *B. Cho*, ***J.P. Chang***, University of California, Los Angeles

ZrO_2 was investigated as a dielectric to replace SiO_2 for dynamic random memory (DRAM) capacitor. ZrO_2 films were deposited on p-Si (100) wafers by ECR-PECVD using zirconium tetra-tert-butoxide ($Zr(OC_4H_9)_4$) as an organometallic precursor, Ar to carry the precursor vapor, and O_2 as oxidant. We used optical emission spectroscopy (OES), Langmuir probe, and quadrupole mass spectrometry (QMS) to characterize the gas phase. Atomic force microscopy results showed that the ZrO_2 surface was very smooth with rms=1.4 Å as long as O_2/Ar was set to over one. X-ray diffraction showed that the films were amorphous. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry indicated that stoichiometric ZrO_2 film was obtained with various amount of carbon incorporation depending on the electron temperature and the O_2 /Ar. We obtained a linear dependence of the carbon content determined by XPS upon the OES intensity ratio of molecular carbon and atomic oxygen. High resolution transmission electron microscopy was used to observe the interfacial layer formation between the deposited ZrO_2 and the substrate Si. Fourier transform infrared spectroscopy was used to investigate the hydrocarbon composition in the film. The electrical properties of the as-deposited ZrO_2 were assessed by forming Al/ZrO_2/Si capacitor structures. We obtained the maximum dielectric constant of 16 at O_2/Ar=1. C-V curves shifted to higher bias voltage with increasing O_2 /Ar, which indicated more negative fixed charges were introduced into the film as we add more O_2 in the gas phase. We observed that the leakage current density decreased drastically with increasing O_2/Ar. ZrO_2 film at O_2/Ar=4 showed $3.3x10^{-6}$ A/cm^2 at equivalent oxide thickness of 25 Å.

PS+TF-WeP3 RF Inductively Coupled Plasma Assisted Re-sputtering Techniques for Step Coverage Control in sub 0.13µm Structures, *P. Gopalraja, S. Rengarajan,* ***J. Forster***, *X. Tang, R. Jauhari, U. Kelkar, A. Chan, M. Schweitzer, K. Miller, A. Bhatnagar, N. Maity, J. Van Gogh, S. Parikh, Z. Xu,* Applied Materials Inc.

A sputter deposition source has been developed that allows the bottom coverage in small structures to be made arbitrarily small, while retaining significant sidewall coverage. This ability is becoming increasingly desirable as copper based back-end metallization schemes in integrated circuits shrink to 0.13µm and below. The reduction in bottom coverage is made possible by utilizing a process, which combines deposition onto and re-sputtering of material from the wafer. The deposition occurs via a partially ionized PVD process, and the re-puttering occurs via a RF inductively coupled plasma assisted re-sputtering process. The hardware components for both deposition and re-sputtering have been integrated into a single chamber. The data presented in this paper will include simulations of plasma characteristics for the re-sputtering process for varying power and pressure conditions, and the correlation of these simulation results with the properties of the thin films deposited. Transmission electron micrographs show bottom coverage arbitrarily close to zero can be achieved in both via and dual damascene structures. Electrical testing on dual damascene structures shows that minimal bottom coverage improves via resistance, and that substantial sidewall coverage improves stress migration and electro-migration properties.

PS+TF-WeP4 Plasma Enhanced Chemical Vapor Deposition of SiO_2 Films from Tetramethylcyclotetrasiloxane and Dimethyldimethoxysilane, ***J. Zhang***, *E.R. Fisher*, Colorado State University

The deposition of SiO_2 films from novel alkoxysilane/O_2 and alkoxysilane/N_2O plasmas has been investigated using tetramethylcyclotetrasiloxane (TMCTS) and dimethyldimethoxysilane (DMDMOS). The films were analyzed with Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy, and spectroscopic ellipsometry. For both the precursors, deposition rates and hydrocarbon incorporation in the SiO_2 films decrease with addition of O_2 or N_2O. High quality SiO_2 films can be deposited when the ratio of oxygen atom to precursor is equal or higher than the reaction stoichiometric ratios, i.e., 20:1 for TMCTS and 14:1 for DMDMOS. The effects of rf power and substrate position in the reactor on film quality are also examined. Gas phase species in these plasmas were studied with mass spectrometry and correlated with film characteristics. Moreover, with the imaging of radicals interacting with surfaces (IRIS) method, the surface reactivity of OH in these plasmas was measured as a function of O_2 or N_2O addition and rf power. The role of OH in deposition of SiO_2 films from TMCTS and DMDMOS based plasmas will be presented and compared to previous results for OH in TEOS/O_2 plasmas.[1]

[1]K. H. A. Bogart, J. P. Cushing, and E. R. Fisher, J. Phys. Chem. B, 101. 10016 (1997).

PS+TF-WeP5 Evaluation of PFC Emission Reduction for PE-CVD Chamber Cleaning with Measurement and Simulation, ***E. Wani***, *K. Kosano, T. Sunada, S. Okura, Y. Mitsui, K. Sakai, T. Beppu,* Research Institute of Innovative Technology for the Earth (RITE), Japan, *A. Sekiya*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of perfluorocarbons and other fluorinated compounds (PFCs) emission from PE-CVD chamber cleaning is one of the urgently required issues in the semiconductor manufacturing for the prevention of global warming. There are mainly three approaches such as the optimization of traditional cleaning processes, the development of alternative gases and the development of alternative cleaning processes. In our recent study, COF_2 has been suggested as a potential alternative cleaning gas.[1] Various methods for the emission reduction have been investigated from the aspects of the alternative gas, process and tools. The process condition optimization is a common requirement to induce best performance for all these investigations. Recently, a simulation tool for the Capacitively Coupled Plasma (CCP) source has been developed and is now commercially available. In this study, the emissions from CCP of C_2F_6 as well as COF_2 have been simulated and the results have been compared with the ones measured by Fourier transform infrared spectroscopy (FT-IR) and Quadrupole mass spectroscopy (QMS), which were equipped after the dry pump. Both results showed that CF_4 emission from COF_2 is less than that of C_2F_6. The discharge in the CVD chamber was also observed using optical emission spectroscopy (OES) and FTIR. The results have been also compared with the ones simulated. This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

[1] Y. Mitsui et al., ISESH 2001, June 17-21, 2001.

PS+TF-WeP6 Eliminating the Hysteresis Effect for Reactive Sputtering Processes, *T. Nyberg,* ***S. Berg***, Uppsala University, Sweden, *U. Helmersson*, Linkoping University, Sweden

Despite that reactive sputtering has existed for more than 50 years, increasing the pumping speed to unrealistically high values is so far the only reported way of eliminating the hysteresis effect for planar magnetrons. The cause of the hysteresis effect is a complex interaction between target sputter erosion and the gettering of the reactive gas on the target and coated surfaces. These relations are not yet fully understood. By computer process modeling, however, we have developed a theoretical model capable of predicting the complex correlations between these

involved parameters. By process modeling it is possible to carry out "virtual processing" to predict processing results for unexplored ways of carrying out processes. By reducing the size of the target sputter erosion zone below a critical value, simulations predicted that it should be possible to completely eliminate the hysteresis. This was also experimentally verified for the reactive sputtering of Al in an argon/oxygen atmosphere. Moreover, there is almost no loss in compound deposition rate as compared to sputtering from a traditionally designed target. Notice that an increase of the total target current using a large sputtering erosion zone will not eliminate the hysteresis. The fundamental explanation to this behaviour as well as experimental verification will be presented.

PS+TF-WeP7 In situ Measurement of C_2 Radical Density in Microwave-Enhanced Methane/Hydrogen Plasma Used for Nanocrystalline Diamond Film Growth, ***M. Hiramatsu***, *K. Kato, K. Ito,* Meijo University, Japan, *C.H. Lau, J.S. Foord*, University of Oxford, UK

Conventional plasma-enhanced chemical vapor deposition (CVD) methods for diamond fabrication normally employ high-pressure (≥10 Torr), and methyl (CH_3) radicals are generally known to be important species for diamond formation. On the other hand, nanocrystalline diamond films were grown using fullerenes in a microwave argon plasma without addition of hydrogen. It was suggested that carbon dimer (C_2) radicals also might play an active role in conventional hydrogen-activated CVD. In the present work, C_2 radical density at the lowest excited state was measured in an ASTeX style conventional microwave plasma reactor with a CH_4/H_2 mixture using absorption spectroscopy. The Xe lamp emitting a continuous spectrum was used as a light source, and transmittance spectra through the plasma ball were obtained around 516.5 nm of (v' =0, v" =0) bandhead of C_2 Swan system. Measurement was carried out under the conditions where nanocrystalline diamond films can be formed. At the typical growth conditions for the microwave plasma-enhanced CVD reactor used for nanocrystalline diamond film formation, the C_2 radical density in the plasma ball was of the order of 10^{12} cm^{-3}. The emission intensity of (0, 0) bandhead of C_2 Swan system was also measured. It was found that the emission intensity correlated linearly with C_2 radical density. C_2 radical density in the plasma ball under the condition where predominantly diamond can be formed was estimated to be 10^{10} - 2 x 10^{11} cm^{-3}.

PS+TF-WeP8 Effect of NO Radical Produced by Additives to PFC on Global Warming during PECVD Chamber Cleaning Using a Remote ICP Source, ***J.H. Kim***, *C.H. Oh,* Sungkyunkwan University, Korea, *S.S. Yoon,* Jusung Engineering Co., Ltd., Korea, *N.-E. Lee, G.Y. Yeom,* Sungkyunkwan University, Korea

N_2, N_2O, and NO were added as additive gases producing NO radical to C_4F_8/O_2 during PECVD(plasma enhanced chemical vapor deposition) silicon nitride chamber cleaning and the effects of these additive gases to the PECVD silicon nitride cleaning have been investigated. For plasma cleaning, a remote ICP(inductively coupled plasma) source was used and cleaning rate, DRE(destruction efficiency), and MMTCE(million metric tons of carbon equivalent) were investigated as a function of gas mixture ratio, working pressure, rf source power, and flow rate. Using this ICP source, high DRE more than 95% could be obtained for all of the investigated conditions due to the high dissociation of the feed gases. Adding N-based additive gases and O_2 to C_4F_8 not only significantly increased the cleaning rate by the surface reaction of NO radical generated by these additive gases but also decreased the MMTCE by decreasing the emitted CF_4 concentration which has the highest concentration among the emitted PFCs (perfluorocompounds) in addition to the high global warming potential. C_xF_y is believed to decrease through the reaction between nitrogen from the additive gases and fluorine or carbon in C_xF_y from the dissociated PFCs. In this experiment, remaining feed gas and emission species such as CF_4, C_3F_8, C_2F_6, COF_2, etc. were detected at the exhaust line during silicon nitride cleaning by FT-IR(fourier transform - infrared spectrometer). Also, F and NO radicals were observed by OES(optical emission spectroscopy) and QMS(quadrupole mass spectrometer) at the chamber.

PS+TF-WeP9 TaN Diffusion Barriers by Chemical-Enhanced Physical Vapor Deposition (CEPVD), ***N. Li***, *J.P. Allain, D.N. Ruzic*, University of Illinois, Urbana-Champaign

Ta and TaN films deposited by physical vapor deposition (PVD) or ionized PVD (iPVD) are widely used as a conducting diffusion barrier layer in ultra-large scale integrated (ULSI) devices to prevent migration of Cu into adjacent dielectrics. While PVD films lack the highly conformal sidewall coverage of chemical vapor deposition (CVD) or metalorganic CVD (MOCVD), they offer high density and low resistivity desired for optimum barrier performance. Since the parameter space of PVD is quite different from CVD, getting the best attributes of both methods is problematic. We describe a novel process called chemically-enhanced physical vapor deposition (CEPVD) that, by the addition of a proper amount of precursor in the vicinity of the substrate, has the potential to deposit films with PVD quality and CVD step coverage. A Ta target is sputtered in a magnetron system with the Ta-containing metal-organic precursor vapor, TBTDET, in combination with a reactive (N_2) carrier gas and an RF-powered secondary ionization plasma. In this preliminary experiment, planar films were deposited on silicon wafers at different pressure, RF incident power, substrate temperature and bias voltage. The ionized metal deposition conveys significant energy to the surface through bombardment, promoting film adhesion and generating films of stable crystallographic orientation. In addition the ion bombardment enhances the impurity volatilization and reduces the substrate temperature needed for chemical decomposition. Deposition rate and ionization fraction are measured using a gridded energy analyzer and a quartz crystal microbalance (QCM). Surface morphology are visualized using SEM and AFM; film composition and microstructure are characterized by XPS and XRD, respectively. Resistivity is evaluated by a four-point probe. Extension of the method to patterned structures is also discussed.

PS+TF-WeP10 Two-dimensional Modeling of Charged Particles Transport in Capacitively Coupled Radio-frequency Discharges, ***A. Salabas***, Instituto Superior Técnico, Portugal, *G. Gousset,* Univ. Paris-Sud, France, *L.L. Alves*, Instituto Superior Técnico, Portugal

Plasma enhanced chemical vapour deposition is often employed to produce chemical active species, using capacitively coupled radio frequency (ccrf) glow discharges driven at 13.56 MHz. Predictions over film deposition rates necessarily pass through the description of charged particle transport in the discharge. The present work describes the transport phenomena in a ccrf reactor using a two dimensional fluid model. The description of charged particle transport is made by solving the continuity and momentum transfer equations for electrons and ions, coupled with Poisson and the electron mean energy equations.[1] The physical model adopts the local mean energy approximation i.e. it computes the electron and energy transport parameters as well as the electron impact collision rates as functions of the electron mean energy. The model writes the electron and energy fluxes in the drift diffusion approximation, including the variation with position of the diffusion coefficient. Ion inertia terms are also considered by generalising the earlier concept of effective electric field.[2] Adequate flux boundary conditions have been employed. The convergence criterion checks the main plasma parameters and assumes steady state solution when relative changes between two subsequent periods are less then 0.001. The model is solved for He, H_2 and SiH_4-H_2 discharges produced within a cylindrical ccrf reactor similar to GEC reference cell, for 68 mTorr - 3 Torr pressures and 100 V - 500 V applied rf voltages. Results concerning non-local phenomena, the influence of silane dilution and reactor geometry are pointed out. In general, comparisons with experimental data indicate that the model improves earlier reported results for some electrical benchmark parameters.

[1] J. P. Boeuf and L. C. Pitchford Phys. Rev E 51 (2) (1995) 1376.
[2] J. D. P. Passchier and W. J. Goedhee J. Appl. Phys. 74 (6) (1993) 3744.

PS+TF-WeP11 Effect of N-based Additive Gases to C_4F_8/O_2 on Global Warming Gas Emission during Silicon Nitride PECVD Chamber Cleaning Process Using a Remote Plasma Source, ***C.H. Oh***, *N.-E. Lee, J.H. Kim, G.Y. Yeom,* Sungkyunkwan University, Korea, *S.S. Yoon,* Jusung Engineering Co., Ltd., Korea

PFCs have been used for CVD chamber cleaning and oxide etching processes. During cleaning and etching processes, the emission of perfluorocompounds(PFCs) into the atmosphere has caused growing concern in the semiconductor industry because of their potential global warming effects. Therefore, the semiconductor industry is proactively seeking ways to reduce PFCs emissions through alternative process chemicals, process optimization, and different abatement technologies including destruction and recovery. In this study, N-based additive gases were added to C_4F_8/O_2 for silicon nitride plasma enhanced chemical vapor deposition(PECVD) chamber cleaning and their effects on the perfluorocompounds(PFCs) emission properties were investigated. We determined an optimum cleaning condition of C_4F_8/O_2 chemistry as a function of processing condition such as additional gas mixture ratio, total gas flow, and working pressure. Under the optimum condition, we quantified the net emission of PFCs during cleaning of silicon nitride using Fourier transform-infrared spectroscopy (FT-IR) and then compared the effects of adding N-based additive gases to C_4F_8/O_2 by evaluating the destruction removal efficiency (DRE) and the million metric tons of carbon equivalent (MMTCE). DRE and MMTCE were calculated by evaluating the volumetric emission. Ar/NF_3 gas mixtures, which are commercially used for PECVD chamber cleaning, were also investigated with the remote plasma source to compare with the results of C_4F_8/O_2/N-based additives gas mixtures. Comparing MMTCE with C_4F_8/O_2/N-based additives and NF_3/Ar in optimum condition, we could obtain similar MMTCE values for each gas mixture. Therefore, it is believed that Ar/NF_3 can be replaced by C_4F_8/O_2/N-

based additive gas chemistry using a remote plasma source for the silicon nitride PECVD chamber cleaning.

PS+TF-WeP12 Low-temperature PECVD Thin Film Optical Waveguides, ***G.T. Dalakos***, *E.M. Breitung*, General Electric Global Research Center

The ability to process inorganic thin film optical waveguides at low deposition temperatures (room temperature to <200C) allows compatibility with a large range of different material types. Notably, these include low-melting point optical polymers. However, most work in inorganic waveguide fabrication has been at high processing temperatures or involved high-temperature post-processing anneal steps which is incompatible with low-melting point materials. We offer insight into performance degradation, especially in regards to the processing of silicon alloy materials at low substrate temperatures in a conventional Plasma-enhanced Chemical Vapor Deposition (PECVD) setup. Optical loss due to interfacial surface roughness and bulk material absorption are focused on and processing methods to reduce both of these are presented.

PS+TF-WeP14 Feature Profile Evolution during Cl_2 and HBr Plasma Etching of Silicon, *M.O. Bloomfield, T.S. Cale,* ***Y.H. Im***, Rensselaer Polytechnic Institute

As demands for improved IC manufacturing continue to increase, topography simulation of the plasma etching process can help engineers develop easier and less costly process recipes. One of the barriers in achieving this goal is the lack of fundamental understanding of the behavior of energetic ions and reactive neutrals at the plasma-solid interface. We present a simulation study of feature topography evolution under Cl_2 and HBr plasma etching using a deterministic approach. In this work, we use the ballistic transport and reaction model that was presented by Cale and Raupp.[1] Fluxes from the plasma directly to the feature surface, from diffuse re-emission of neutrals from the surface, and from both specular and non-specular reflection of ions are considered. To consider the angular and energy dependence of the etch rate, we use the work of Chang and co-workers.[2] In order to capture the bimodal shape of ion energy distribution, we regard the bombarding ions as the sum of independent monoenergetic species. We consider the ion angular distribution of each monoenergetic species, so that the effect of ion energy distribution on the shape of feature profile can be investigated. We compare the shape of etched feature profiles, some of which exhibit microtrenching, to experimental data for Cl_2 and HBr plasma etching. Our simulations show that the difference in etched profiles can be regarded as due to the different characteristics of the specular reflection and the dependence of the etching yield on incident angle for Cl_2 and HBr plasma. Simulation results are compared with experimental data and Monte Carlo based simulation from the literature.

[1] T.S. Cale and G. B. Raupp, A Unified line-of-sight model of deposition in rectangular trenches, J. Vac. Sci. Technol. B 8 (6), 1990

[2] Jane P. Chang, Arpan P. Mahorowala, and Herbert H. Sawin, Plasma-surface kinetics and feature profile evolution in chlorine etching of polysilicon, J. Vac. Sci. Technol. A 16, 1998

PS+TF-WeP15 Plasma Damage Reduction in PZT Thin Films Etched by Inductively Coupled Plasma, ***K.T. Lim***, *D.P. Kim, K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

Ferroelctric lead zirconate titanate ($Pb(Zr,Ti)O_3$) 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. During the dry etching, the defects, such as physical damage and chemical residue contamination and decomposition, will change the near surface region of the material that is exposed to the plasma and degrade ferroelecric and electrical properties. In this study, PZT thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates by sol-gel processes. Pt top electrodes were deposited on PZT thin films by using rf magnetron sputtering. SiO_2 was deposited on Pt top electrodes. SiO_2 layer was etched in CF_4/Ar inductively coupled plasma with PR mask. We continued etching Pt/PZT/Pt layer without removing PR and SiO_2 patterns. PZT thin films were etched with Ar/Cl_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 Cl_2/Ar plasma. The ferroelectric and electrical properties were measured with a precision workstation. We obtained stable value of remanent polarization and good fatigue resistance for PZT with SiO_2 mask as compared with Pt dot, which was used as physical mask during etching process. The structural damages to the near surface of PZT are evaluated by transmission electron microscope (TEM) and x-ray diffraction (XRD). The chemical deformation of etched surface was surveyed x-ray photoelectron spectroscopy (XPS), electron probe micro analyzer (EPMA), auger electron spectroscopy (AES) and TEM-EDS.

PS+TF-WeP16 Effects of Substrate Temperature on the Etching of Silver Films using Inductively Coupled Halogen-based Plasmas, ***S.D Park***, *Y.J. Lee,* Sungkyunkwan University, Korea, *S.G. Kim, H.H. Choe, M.P. Hong,* Samsung Electronics, Korea, *G.Y. Yeom*, Sungkyunkwan University, Korea

Silver(Ag) is one of the potential materials in thin film transistor liquid crystal display (TFT-LCD) because of its lowest bulk resistivity of all metals at room temperature and high reflectivity. Also, it is one of the attractive candidates for the intergrated circuit(IC) manufacturing. Currently, Ag etching is performed using wet etching methods, however, for the fabrication of the high resolution display devices, the use of plasma etching process is indispensable. In reality, there are several problems to be solved before Ag plasma etching to be applied to TFT-LCD processing. The main problems are the formation of involatile etch products, low etch rates, and high surface roughness after removing the etch products. For example, many works on Ag etching using halogen-based plasma have been studied, however, slow etch rates lower than 100nm/min and a thick involatile Ag etch products remaining during the etching were reported. Therefore, in this study, using an inductively coupled halogen-based plasma, the effects of substrate temperature were investigated to obtain higher Ag etch rates without remaining any involatile etch products. The results showed that when the substrate temperature was increased above 70°, the etch rate higher than 250nm/min could be obtained and, when Ar is added to halogen plasma, Ag etch products were effectively removed during the etching because of the increase of sputtering effect of etch products. To understand have the Ag etching characteristics, the optical emission spectroscopy(OES) and X-ray photoelectron spectroscopy(XPS) have been used and measured as a function of gas combination and substrate temperature. Also, a scanning electron microscope(SEM) was used to observed as-etched Ag surfaces.

PS+TF-WeP18 A Study of Sapphire Etching Characteristics using Magnetized Inductively Coupled Plasmas, ***C.H. Jeong***, *D.W. Kim, H.Y. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

Sapphire substrate is attractive material because of its superior mechanical and corrosion property. It has been widely used as the substrate for GaN epitaxial growth and as insulating layer due to its high chemical stability, thermal stability, and dielectric property. On the other hand, it is known to be difficult for other processing such as etching and cutting due to the chemical and high thermal stability, the high hardness of sapphire itself, and the differences in the crystal orientation for GaN on sapphire. In this study, (0001) sapphire wafers were etched using magnetized inductively coupled plasmas(MICP) and their etch characteristics were compared with those by non-magnetized conventional inductively coupled plasmas(ICP). The use of Helmholtz type axial electromagnets around the chamber wall increased the sapphire etch rates while decreasing etch uniformity. By using both multi-dipole permanent magnets and axial electromagnets around the chamber wall, the etch uniformity could be improved while maintaining high sapphire etch rates. The sapphire etch rates close to 700nm/min which are higher than those etched using the conventional ICP could be obtained with optimized MICP conditions. The effects of etch parameters such as axial electromagnetic field(0 - 40Gauss), inductive power(600 - 1600Watts), and bias voltage(-100 - -300Volts) on the sapphire etch characteristic such as etch rates and etch selectivity over photoresist were investigated. The gas chemistry were maintained at 81%BCl_3/9%HBr/10%Ar, respectively. The etch mechanism of sapphire in MICP was investigated by plasma diagnostics using optical emission spectroscopy(OES) and quadrupole mass spectrometry(QMS) during the sapphire etching and by surface analysis using X-ray photoelectron spectroscopy(XPS) after the etching. The etch profile was observed as a function of process parameters by scanning electron microscopy(SEM) before and after etching the samples.

PS+TF-WeP19 Improvement of Etching Sub-micron Photonic Structure by Enhanced-inductively Coupled Plasma (E-ICP), *S.B. Jo,* ***B.H. O***, Inha University, Rep. of Korea, *Y. Fainman*, University of California, San Diego, *S.G. Park, S.G. Lee, E.H. Lee*, Inha University, Rep. of Korea

Photonic crystals have attracted broad range of interests due to fascinating control power of light propagation in photonic devices. As it is important in photonic devices to have optical surface smoothness and high accuracy of critical dimensions, it is not simple to fabricate photonic crystals with sub-micron period. It is required to minimize surface smoothness and to have highly anisotropic etch profile in order to achieve high fidelity fabrication of photonic crystal structures. In this study, we have fabricated a silicon-oxide sub-micron grating for 1D-photonic crystal structure by plasma etching method. A simple periodic grating structure with a period of sub-wavelength of a light is a kind of one dimensional photonic crystal with a special purpose. The characteristics, such as etch profile and surface roughness, are improved in enhanced inductively coupled plasma (E-ICP)

technique compared to normal ICP technique. PMMA as a mask of a fine-grating patterning is patterned by a E-beam lithography. Sub-micron grating patterns have been successfully transferred into silicon-oxide layer with high etch rate over 350 nm/min, at the optimized condition of an E-ICP mode. The vertical angles are about 90Â° and the surface roughness is less than 20 nm as seen in a scanning electron microscope (SEM) images.

PS+TF-WeP20 Inductive Coupled Cl_2/Ar Plasma: Experimental Investigations and Modeling, ***A.M. Efremov***, Ivanovo State University of Chemistry & Technology, Russia, *D.P. Kim*, *C.I. Kim*, Chung-Ang University, Korea

Inductively coupled plasma in Cl_2/Ar mixtures is a widely used in microelectronics technology. The main aim of the current work was to investigate the influence of external process parameters (gas pressure and flow rate, input power density, mixture content) on internal electro-physical properties (EEDF, electron drift rate and average energy) and on a kinetic characteristics of neutral and charged active particles formation and decay (kinetic and transport coefficients). Investigations were carried out in ICP 13.56 MHz system under such condition as: gas pressure 10 - 30 mTorr, total gas flow rate 10 - 20 sccm and input power density 0.1 - 0.2 W/cm^3). Analysis was carried out using both experimental and mathematical modeling technique. Experimental part included investigations using OES spectroscopy and actinometry, langmuir probe measurements and QMS analysis. Modeling algorithm was based on the simultaneous self-consistent solution of Boltzmann kinetic equation together with the balance kinetic equation of neutral and charged particles formation and decay in a quasi-steady-state approximation. A main mechanisms supporting chlorine atoms formation and decay both for volume and heterogeneous processes were analysed including a stepwise dissociation involving an excited "heavy" particles (Ar metastable atoms). A stationary mass content of plasma volume including neutral (ground-state and excited atoms and molecules) and charged (electrons, positive and negative ions) was determined under the various external process conditions.

PS+TF-WeP22 Improvement of ITO Etch Rate and Uniformity by Enhanced-ICP Technique, *C.W. Kim*, ***S.B. Jo***, *B.H. O*, *S.G. Park*, Inha University, South Korea

Indium-tin-oxide(ITO) is now being used widely as a transparent electrode with high optical transmittance and excellent electrical conductivity. As the wet etch technique of ITO has several problems, such as isotropic etch profile and etch rate dependent film characteristics, dry etch technique has been applied to form ITO film-electrodes. Although the dry etch technique of ITO with organic gas chemistry provides good anisotropic etch profile, it has the problem of low etch rate. And as the size of applicable substrate, such as for the flat panel display(FPD), increases, the uniformity of etch rate on large area becomes one of the most important issues. Here, we report improved etch characteristics of ITO on large area by applying the 'Enhanced-ICP'(Inductively Coupled Plasma) technique with an appropriate design of experiment (DOE), based on Taguchi method, to obtain better etch rate with organic gases. The unit ICP antenna for large area plasma source is arrayed to form 2x2. The etch rate of ITO with E-ICP operation showed improvement of about 50% than normal-ICP operation, as consistent to the previous report for the photoresist etch by E-ICP operation. A better etch uniformity is also obtained on 350x300mm substrate with E-ICP operation.

PS+TF-WeP23 Modeling of Etch Profiles in RF biased Inductively Coupled Plasma Etching Reactor, ***C.D. Wang***, *B. Markland*, *D. Malanaric*, *E. Brown*, *D. Galley*, ATMEL, *B. Abraham-Shrauner*, Washington University, *R. Hoekstra*, Sandia National Laboratories

Knowledge of the ion angular distribution at the wafer plane in an etching plasma is critical for modeling the etching profiles. The etching profile is an evolution of etch surface in time. The evolution equation can be expressed in terms of etch rate. This paper illustrates that the etching profile can be obtained by considering both the ion energy distribution (IED) and ion angular distribution (IAD). These distributions were generated using the Hybrid Plasma Equipment Model and Plasma Chemistry Monte Carlo Model for a Lam TCP plasma etching reactor. The points from the distribution function simulations are divided into different sets in terms of incident angles of ions. Due to the noisy characteristics of simulated data, a smoothing technique is implemented. Each set of smoothed data is fitted with multiple terms of the analytical expression for the drifting Maxwellian distribution functions. These etch rates manifest a proportional relationship with the ion energy flux of experimental evidences by Ding et al.. A statistical optimization technique is utilized here for extracting three parameters: ion temperature, ion density and ion drift energy from each set of the ion drifting Maxwellian distribution functions. By using these crucial parameters, an etch profile is obtained.

PS+TF-WeP24 Impact of Pattern Density on Characterization of Critical Dimension, ***X. Xu***, *E. Croffie*, *M. Garza*, LSI Logic Corporation

The plasma etch of polysilicon is the most critical step in the fabrication of integrated circuits with submicron features since the critical dimension of polysilicon, which is typically used as gates, affects the speed performance of microelectronics devices. The characterization of polysilicon plasma etch can be varied by a global pattern density (called the loading effect) and a local pattern density (called the microloading effect). The etch variations, caused by the pattern density, depend on the specific plasma sources and tool configuration. In this work, silicon wafers patterned with photo resist on a stack of N-doped polysilicon and silicon dioxide have been etched on Lam 9400 DFM etching system in order to investigate the effects of pattern density on critical dimension (CD) and CD bias. The global density is obtained by varied dummy sizes and densities. The local effect is obtained by a large area with a certain polysilicon density and narrow isolated and dense lines at different distances from the large area. It has been found that the impact of global and local polysilicon densities with our new recipe on the tool is small compared to our old technology. In addition, the corresponding plasma chemistries have been studied by the Hybrid Plasma Equipment Model (HPEM).

PS+TF-WeP25 Effects of Ion Bombordment on Developed Photoresist during RIE Processes for sub 0.25 micron Semiconductor Devices, ***M. Naeem***, *R. Wise*, IBM Microelectronics, *T. Wang*, Cypress Semiconductors, *G. Worth*, *D. Dobuzinsky*, IBM Microelectronics, *Z. Lu*, Infineon Tech, *H. Abdul-Ridha*, Conextent

The use of advanced resist systems has become necessary for lithography in processing of advanced (sub 0.25 Âµm) 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+TF-WeP26 Characterization of RIE Lag Scaling In Oxides, ***D.L. Keil***, Lam Research Corporation

Recent advances in ultra large-scale integration (ULSI) have typically depended on reductions in etched feature size. This has motivated efforts to find etch processes that will precisely etch increasingly smaller features while retaining the ability to etch larger features. As feature sizes push below 0.25 µm, reactive ion etch (RIE) lag control becomes increasingly important. Knowing how RIE lag scales with feature size for a given process aids in determining if that process must be discarded and a new one developed. In those situations where a process cannot be discarded, an understanding of RIE lag scaling aids in predicting fabrication difficulties for a given device design. Using a minimal set of initial assumptions, it is shown that a relationship can be derived which relates etch rate to the time development of the feature aspect ratio. It is then shown that this relationship can be used to derive an expression for the etch depth as a function of time and feature size. The assumptions made are justified by phenomenological observation rather than by an assumed mechanism. This approach enhances the generality of the results obtained, thus making them useful for a variety of practical etch engineering applications.

PS+TF-WeP27 The Etching Mechanism of Au Thin Films in Cl_2/Ar High Density Plasma, ***Y.S. Chang***, *D.P. Kim*, *C.I. Kim*, *E.G. Chang*, Chung-Ang University, Korea

Au is employed extensively in the electrodes of high dielectric capacitors or in compound semiconductor devices, principally because of its high electrical conductivity and its property of relative chemical inertness. Since the report of Au thin film etching has a few, we studied the etch characteristics of Au thin films by using high density plasma etching system. In the study, Au thin films were etched with a Cl_2/Ar gas combination in an inductively coupled plasma. The experiment was done by controlling the etching parameters such as gas mixing ratio, radio frequency power, direct current bias, and chamber pressure. The surface reaction of the etched Au thin films was investigated with x-ray photoelectron spectroscopy (XPS) using narrow scan spectra. Ar ion bombardment is more dominant than chemical reaction between Au and Cl. The results of secondary ion spectrometer (SIMS) analysis were the same as results of XPS analysis. In addition, optical emission spectroscopy (OES) were investigated to analyze radical density of Cl and Ar in plasma. The profile of etched Au investigated with scanning electron microscopy (SEM).

PS+TF-WeP28 Reduction of Particle-contamination in Plasma Etching Equipment by Dehydration of Chamber Wall, ***N. Ito***, *F. Uesugi, T. Moriya,* NEC Corp., Japan, *M. Matsumoto,* Lam Research Co., Ltd., Japan, *S. Liu,* Lam Research Corporation, *Y. Kitayama*, Lam Research Co., Ltd., Japan

For reduction of particles sticking on the wafers in the poly-gate (WSi/poly-Si) etching by real transfer couple d plasma (TCP) equipment, we have investigated the behavior and the outbreak of particles above the wafers by using lase r light scattering method. Numbers of particles on the wafers were also investigated by wafer-level inspection machines. Most particles were observed at rf power turned-off in case of the process gas containing fluoride. The main compositio n of particles were Al and F. And upside of the process chamber wall coated with Al_2O_3 was corroded. Therefo re it was inferred that these particles were generated by a reaction of the fluoride gas and Al_2O_3 surface. Moreover, numbers of particles above and on wafers were drastically increased after the wet cleaning of the chamber wall . It showed that the reaction of generating particles was activated by moisture. From the knowledge, dehydration process inserted after wet cleaning of a process chamber achieved the particle-contamination reduction. In the conventional mai ntenance, it took 30 hours to reduce the number of particles until acceptable quantity after wet cleaning. However it wa s shorten to 2 hours by inserting dehydration process.

PS+TF-WeP29 Shallow Trench Isolation Etch for Sub 0.10 µm Applications, ***S.M. Williams***, *J. He, M. Shen,* Applied Materials

As feature size continues to shrink to sub 0.10µm and below, photoresist thickness is becoming steadily thinner, and the migration to 193nm resist is beginning. We have developed resist mask and hard mask etch processes, which address the challenges posed by these small feature sizes. Both processes are in situ, with the mask open and trench etch performed in the same chamber, increasing throughput and lowering the cost of ownership. For customers who require near zero nitride loss, the resist mask approach allows the continuation of current integration schemes; by protecting the nitride throughout the trench etch. The process is tunable from 78-88 degrees, and incorporates both top corner and bottom corner rounding in order to minimize leakage current and stress related defects. The resist mask process will eventually run into limitations when resist thicknesses approach 3000Å, especially when 193 nm resist is used, driving STI etch toward the hard mask approach. For customers making a transition from a resist to a hard mask STI etch, it is important to maximize the selectivity to the nitride hard mask in order to minimize the impact on the integration scheme. We have developed a hard mask process, which is highly selective to nitride (>40:1) and tunable from 78-88 degrees. Bottom corner rounding and top corner rounding schemes are incorporated. In addition, the process is HBr free, eliminating the corrosion associated with Br condensation.

PS+TF-WeP30 Silcon Etching in High-Denisty Plasmas, Revisited, ***A.S. Orland***, *R. Blumenthal*, Auburn University

The ECR-microwave plasma etching of silicon with chlorine is revisited using the enhanced capabilities of supersonic pulse, plasma sampling mass spectrometry. Using a new orthogonal injection time-of-flight mass spectrometer, it is now possible to measure the relative concentrations of both etch products, such as SiCl, $SiCl_2$, $SiCl_3$, and sputtered species, such as Si_2Cl, Si_2Cl_2, and distinguish them from species formed in the gas phase as a function of plasma conditions.

Plasma Science
Room: C-103 - Session PS+BI-WeA

Plasma Processing for Biocompatible Surfaces

Moderator: H.J. Griesser, University of South Australia

2:00pm **PS+BI-WeA1 Application of Plasma in Tissue Engineering**, ***R.D. Short***, *D.B. Haddow, S. MacNeil, R.A. Dawson, D. Barton, S. Fraser*, University of Sheffield, UK **INVITED**

A novel device which comprises an acrylic acid plasma polymerized carrier substrate, which supports the attachment and release of human keratinocytes, has been used to successfully treat non-healing (chronic) skin wounds. In proof of concept studies, weekly delivery of keratinocytes, initially obtained from a small 2x1cm biopsy and expanded up many hundred fold, have promoted healing in diabetic foot ulcers and other indications. In this paper we explain the rationale behind this therapy and review the results (to date) from the treatment of the first seven patients. Although the "mode of action" of the device is still to be fully understood, the role the plasma polymer plays in promoting cell attachment and detachment is key to the success of the device. The physical and chemical nature of the plasma polymer has been explored in some detail, and to a first approximation, we are able to describe the features of the plasma polymer that promote cell attachment and speculate on why cells transfer to an in vitro human dermal wound bed model. By means of a multi-technique approach (mass spectrometry,quartz crystal microbalance, ion flux probe, x-ray photoelectron spectroscopy, secondary ion mass spectrometry) we have begun to unravel the processes by which the acrylic acid plasma polymer grows. A case is made for better understanding of plasma polymer growth mechanisms, rather than treating the plasma polymerization process as a "black box" that produces materials with desired properties.

2:40pm **PS+BI-WeA3 Can Plasma Polymerised Surfaces Promote the Co-culture of Human Dermal Fibroblasts and Human Epidermal Keratinocytes in the Tissue Engineering of Skin?**, ***M.C. Higham***, *S. MacNeil, R.D. Short*, University of Sheffield, UK

Within the field of tissue engineering there is a need to develop new approaches to achieve effective wound closure in patients with extensive skin loss or chronic ulcers. Plasma polymers are synthetic surfaces capable of influencing and controlling cell physiology either directly or through an adsorbed protein layer. This project exploits the well-known interdependency of epithelial keratinocytes and stromal fibroblasts in conjunction with plasma surface technology. The aim of my project is to produce a chemically defined surface, which with the aid of a feeder layer of lethally irradiated dermal fibroblasts will improve the performance of the keratinocyte cell. Unable to divide yet remain physiologically active, irradiated fibroblasts aid keratinocyte attachment and proliferation from which sub-confluent cells can be transferred to wound bed models. Plasma co-polymers of acrylic acid/octa-1,7-diene have been prepared and characterised using X-ray photon spectroscopy (XPS). The fibroblasts and keratinocytes were cultured on plasma polymer coated 24 well plates. Cell attachment and proliferation were assessed using MTT-ESTA and DNA assays. The performance of both cell types on the plasma polymer surfaces was compared to Tissue Culture Plastic (TCPS) and Collagen I, plus a negative control of a pure hydrocarbon layer. A pure acrylic acid surface, fabricated at a power of 10W and containing 9% carboxylate group was found to promote both fibroblast and keratinocyte attachment and proliferation and permit the co-culture of keratinocytes with irradiated fibroblasts. The performance of this surface was comparable to collagen I, a well-established substratum for the attachment of keratinocytes. Current work is examining the potential of plasma polymer surfaces within the field of tissue engineering for transfer of keratinocytes onto an in vitro wound bed model and thereafter clinical trials.

3:00pm **PS+BI-WeA4 The Role of Reactive Neutral and Ionic Species in the Deposition of Organic Thin Films from an Isopropyl Alcohol and Argon Plasma**, ***D.C. Guerin***, National Research Council, Canada, *V.A. Shamamian*, Naval Research Laboratory

We present the measurements of neutral species in an argon/isopropyl alcohol (iPrOH) plasma, using appearance potential mass spectrometry. IPrOH is a potential precursor for the cost-effective plasma deposition of non-fouling surfaces. This work complements previous research on the ionic character of the plasma. It had been discovered that tuning the plasma pressure and power caused large variations in the dominant ionic reactions. The resulting changes in the chemical nature of the ionic flux were reflected in the functional character of the deposited films. A significant flux of neutral radicals was detected at the deposition surface at low plasma pressure. However, at higher pressures the plasma region was more remote and the neutral radicals were completely attenuated. The attenuation mechanism was determined to be reaction with the precursor. For example, the methyl radical abstracts hydrogen from iPrOH. Thus, as the pressure increases, the methyl radical flux evolves into a flux of methane. Mean free path (MFP) calculations for hydrogen abstraction agree with the experimental results. At low pressures, the reactive MFP is larger than the chamber geometry. At higher pressures, the reactive MFP is much smaller than the distance between the plasma and deposition surface. The ability of the reactive ions to diffuse from the remote plasma to the deposition surface is explained as being due to charge exchange limitations. The radical species generated have lower ionization energies than iPrOH or argon. Thus, the radical ions are energetically unable to react with the main species in the plasma. In contrast, the flux of ions with ionization energy greater than that of iPrOH, such as argon and methane, is highly attenuated at higher pressures. These results provide some context to competing claims as to the importance of neutrals and ions in deposition from molecular plasmas.

3:20pm **PS+BI-WeA5 Plasma Micropatterning for the Spatially Controlled Adsorption of Proteins**, ***J.D. Whittle***, *R.D. Short, D. Barton, A.G. Shard*, University of Sheffield, UK

Many biological interactions are surface mediated, for example protein adsorption and subsequent cell adhesion. In vitro it may be desirable in a number of applications to exert spatial control over these interactions. i.e. Limiting the attachment of cells to particular surface regions. We investigate the use of masks as a method of fabricating surfaces with patterned chemistry by plasma polymerisation, with feature sizes down to around 10µm. We utilise imaging secondary ion mass spectrometry (SIMS) and fluorescent light microscopy to visualise these chemical patterns. We also show how these chemical patterns affect the adsorption of proteins, not only in terms of the the amount of adsorbed protein, but also their conformation. A natural extension of depositing well-defined regions of chemistry (patterns) is to be able to fabricate regions of controlled chemical change (gradients), the properties of which vary continuously along the length of the deposited feature without any sharp transitions. We show how plasma polymerisation may be used to deposit chemical gradient surfaces with chosen endpoints (for example, a gradient running from a hydroxyl though to an amine dominated surfaces), and profile (for example, linear, sigmoidal etc.) by careful manipulation of the plasma composition and deposition surface during the treatment. These gradient surfaces can be used to examine the affect of changing a particular surface parameter (for example, the surface concentration of amine functionalities) on protein adsorption.

3:40pm **PS+BI-WeA6 Chemical Surface Micropatterning by Plasma and VUV Photochemical Modification of Polymers for Controlled Cell Culture.**, ***N.A. Bullett***, *F.E. Truica-Marasescu, M.R. Wertheimer*, Ecole Polytechnique, Canada

The three dimensional nature of the biomolecular environment in contact with cells has an important influence on the initiation and control of cell processes such as adhesion, migration, growth, protein secretion and gene expression. Traditionally, cell culture uses homogeneous substrates with no control over the biochemical and topological features in the immediate vicinity of the cells. The shape of mammalian cells is determined by the interaction of cell contact receptors with other cells or extracellular matrix proteins. Regulation of the shape of cells may enhance the function and differentiation of the cells. Surface modification of polymeric materials by low-pressure plasma and VUV photochemical treatment provides a convenient route to the fabrication of well defined chemically functionalised surfaces. A variety of functional groups may be introduced into the polymer surface, including amine and hydroxyl. Using these techniques it is possible to engineer surfaces that have a wide variety of applications in biomaterials technology, such as cell and protein adhesive surfaces or non-fouling surfaces. Complex micropatterns of chemically different regions have been produced by the selective functionalisation of the polymer using photolithographically defined masks. By this method, chemically distinct regions are produced at the micrometer scale, with a third dimension being provided by nanoscale topographical features. This three dimensional environment, on the nano- or micrometer scale, provides a complex but controllable surface for the culture of many different cell types. Characterisation of the micropatterned surfaces has been performed by XPS, FTIR, imaging TOF-SIMS and fluorescence microscopy. The surfaces have subsequently been used to study the attachment and growth of various cell types, for example bone-derived cells with orthopaedic applications.

4:00pm **PS+BI-WeA7 Study of Adhesion Mechanism of Protein-based Hydrogel to Plasma Treated Polymer Surface**, ***O. Zabeida***, Ecole Polytechnique of Montreal, Canada, *M.-P. Faure*, Bioartificial Gel Technologies, Canada, *J.E. Klemberg-Sapieha*, *L. Martinu*, Ecole Polytechnique of Montreal, Canada

Biodegradable protein-based hydrogels (solid water solutions, SWS™) are a new class of biomaterials with great potential for use in numerous pharmaceutical and medical applications. Since they may contain up to 96% of water, some SWS are rather fragile and difficult to handle and manipulate. This problem can be solved by applying appropriate polymer backings; the latter one has to be surface treated in order to enhance the hydrogel's adhesion. We found that plasma modification of polymer backings can lead to a 20-fold increase of the adhesion force between the SWS and the polymer surface. In the present work we have applied a multitechnique surface analytical approach, including infrared spectroscopic ellipsometry, XPS, AFM, and TOF-SIMS, to investigate the adhesion mechanism of hydrogels to low pressure plasma-treated polymers (polypropylene, polyethylene terephthalate, and others). The surface chemical structure and morphology are correlated with the adhesion force of the SWS. The results suggest that introduction of amine groups plays a major role in the adhesion improvement, while the surface roughening, polymer chain scission and surface electric charge should also be considered.

4:20pm **PS+BI-WeA8 Permanent Hydrophilic Modification of Porous Membranes Using Low-Temperature Plasmas**, ***D.S. Wavhal***, *E.R. Fisher*, Colorado State University

We have explored the use of low-temperature plasmas to modify porous polymeric membranes with the goal of creating hydrophilic surface throughout the membrane structure. One motivation for this work is to decrease membrane fouling and to eliminate the need for wetting agents in a variety of applications. Porous polyethersulfone (PES) membranes were modified by CO_2 plasma treatment and Ar-plasma treatment followed by grafting of hydrophilic monomers (acrylic acid and acrylamide), in the vapor phase. Plasma treatment and plasma induced grafting rendered a complete hydrophilicity to the entire PES membrane cross section. The hydrophilicity of the membranes treated with only the Ar-plasma is not, however, permanent. In contrast, the PES membranes treated with CO_2 plasma and the grafted membranes are found to be permanently hydrophilic (for a minimum of six months). Chemical changes to the modified PES membranes were determined with FTIR and XPS measurements. Furthermore, water bubble point measurements and electron microscopy results reveal that pore sizes of the modified membranes are slightly affected. The pore sizes of the grafted membranes at higher grafting yield are slightly decreased. Due to incorporation of polar functionalities, the glass transition temperature (T_g) of modified membranes also increases. A moderate change in tensile strength of the modified membranes was observed. Most importantly, the surface of the modified membrane are less susceptible to absorbtion by bovine serum albumin (BSA) proteins and give greater flux recoveries. This suggests that the protein fouling layer is reversible because of hydrophilic nature of the modified membranes.

4:40pm **PS+BI-WeA9 Acrylic Acid Films Deposition by RF PACVD: Relation between Monomer Fragmentation and Surface Properties**, *P. Rossini*, *G. Ceccone*, European Commission, Joint Research Centre, Italy, *K. Jandt*, University Jena, Italy, ***F. Rossi***, European Commission, Joint Research Centre, Italy

The present study deals with the deposition of acrylic acid thin films by radio frequency plasma assisted chemical vapour deposition. The experiments have been carried out in a cylindrical capacitively coupled plasma reactor at different electrical powers (5-60 Watt), in order to optimise the precursors fragmentation and to tune selectivity and stability of the deposited polymers. In situ diagnostics (Mass Spectrometry and Optical Emission Spectroscopy) have been used in order to control the deposition processes and analyse the fragmentation steps. The films have been characterised with X-Ray Photoemission Spectroscopy (XPS) and Fourier Transformed Infrared Spectroscopy (FTIR). Surface energy of the coatings has been determined by contact angle measurement. The protein adsorption kinetics has been evaluated with the Quartz Crystal Microbalance (QCM-D) with HSA. The results demonstrate a strong link between monomer fragmentation in the plasma and functional groups retention in the films. By increasing the RF power, the COOH concentration in the films (XPS and FTIR) as well as hydrophylicity, hydrogen bondings and acid-base character decrease while the CO concentration in the plasma phase (MS and OES) increases. At the same time, the dispersive and the polar components of the surface free energy increase. These surface properties have a strong influence on the protein attachment kinetics, as determined by QCM measurements.

Plasma Science
Room: C-105 - Session PS+MM-WeA

Feature Profile Evolution /Plasma Processing for MEMS
Moderator: A. Kornblit, Bell Labs, Lucent Technologies

2:00pm **PS+MM-WeA1 Plasma Molding Over Trenches and Resulting Ion/Fast-neutral Distribution Functions**, ***D. Economou***, *D. Kim**, University of Houston

Plasma molding over surface topography finds applications in MEMS microfabrication, neutral beam sources, plasma extraction through grids, and plasma contact with internal reactor parts (e.g., wafer chuck edge). The flux, energy and angular distributions of ions incident on the substrate are of primary importance in these applications. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface topography. When the sheath thickness is comparable to or smaller than the feature size, the sheath tends to "mold" over the surface topography. A two-dimensional fluid/Monte Carlo simulation model was developed to study plasma "molding" over surface topography. The radio frequency (RF) sheath potential evolution, and ion density and flux profiles over the surface were predicted with a self consistent fluid simulation. The trajectories of ions and energetic neutrals (resulting by ion neutralization on surfaces or charge exchange collisions in the gas phase) were then followed with a Monte Carlo simulation. Ion flow and energy and angular distributions of ions and energetic neutrals bombarding the walls of a trench will be reported. Emphasis will be placed on high aspect ratio features of interest to MEMS and neutral beam sources. Simulation results will be compared with experimental data, taken at Sandia National Labs, on ion flux and ion energy and angular distributions at the bottom of trenches. Work supported by the National Science Foundation and Sandia National Laboratories.

2:20pm **PS+MM-WeA2 Physically Based Modelling of High-Density-Plasma-CVD on the Feature Scale**, ***G. Schulze-Icking***, *A. Kersch*, Infineon Technologies AG, Germany, *A. Knorr*, Infineon Technologies, *A. Hausmann*, *J. Radecker*, Infineon Technologies Dresden GmbH & Co. OHG

Due to its low thermal budget and its highly directional deposition HDP-CVD of SiO2 has become an important process in IC fabrication. In order to study (and ultimately improve) the HDP-CVD process we have developed a physically based model for feature scale simulations. This model has been implemented into our custom Topography Simulator "Topsi" and extensive studies of the HDP-CVD process have been performed. In this presentation we give a survey of our simulation results and compare them to experiments. The model we propose retains the characteristics of a complex reactor scale model published by Meeks et al.[1] and extends it to the feature scale. A key aspect of both models is a "structural passivation" of the surface due to the chemisorption of gas phase precursors. In contrast to conventional CVD (at much higher temperatures) in HDP-CVD this passivation is removed by cations striking the surface. Accordingly ions not only sputter surface material but also are responsible for its directional deposition. The final topography therefore is the result of simultaneous neutral deposition/passivation, ion induced activation, and sputtering. It is well known[2] that the sputtering yield crucially depends on the ion energy and the angle of incidence. This probably also applies to ion induced surface activation, but very little is known about its energy and angular dependence. We therefore have performed deposition experiments and compared the final topography to simulations performed using our new model. With the derived set of parameters we are now able to predict the surface evolution as a function of process conditions. This is a major improvement over a more empirical model proposed by Conti et al.[3]

[1] E.Meeks et al.; J.Vac.Sci.Techn. A, 16, pp 544 (1998)
[2] C.Abrams et al.; J.Vac.Sci.Techn. A, 16, pp 3006 (1998)
[3] R.Conti et al.; DUMIC Conference (1999).

2:40pm **PS+MM-WeA3 Micro- and Nano-Fabrication Technology for High Aspect Ratio Micro-Electromechanical Systems (MEMS)**, ***S.W. Pang***, The University of Michigan **INVITED**

For many applications in micro-electromechanical systems (MEMS), having high aspect ratio sensors or actuators can improve performance, increase sensitivity, and lower power consumption. Micro- and nano-fabrication technology can be used to generate these high aspect ratio MEMS. Etch rate, profile, selectivity, and uniformity could vary as aspect ratio becomes higher since plasma etching characteristics depend on aspect ratio of microstructures. These variations could affect MEMS performance.

* PSTD Coburn-Winters Student Award Finalist

In this talk, key issues to provide precise control in MEMS fabrication by plasma processing will be discussed. High aspect ratio MEMS including micromirrors for optical switching arrays, submicrometer resonators for accelerometers, sharp tips for emitters or scanning probes, and microheaters for micro-gas chromatography systems will be reviewed.

3:20pm **PS+MM-WeA5 Critical Tasks in the High Aspect Ratio Silicon Dry Etching for MEMS**, ***I.W. Rangelow***, University of Kassel, Germany **INVITED**

Microscopically uniform anisotropic etching of semiconductor layers is a critical step in ME(O)MS and ULSI circuit fabrication. The non-ideal etched feature limits density, yield and reliability of these devices. Artefacts such as RIE-lag, notching, sidewall bowing, micro-trenching, and mask facetting are typically accompaniment effects occurring during the etching high aspect ratio features in silicon. Because etch rates and the shape of etched features depend on circuit layouts-design, considerable effort have to be spent in the near feature to understood all common single and simultaneous phenomena during the high aspect ratio dry etching. The development of effective manufacturing processes requires a fundamental understanding of the factors, which determine etched feature shape. Gas reactivity, pressure (affecting ion bowing in the sheath due to scattering with neutrals), ion, electrons and reactant transport to the surface, and product transport away from the surface, have been identified as the key factors that control the microscopic etching uniformity in high aspect ratio etching. The choice of these can cause numerous secondary aspect ratio-dependent effects. The modelling of the most significant effects as RIE-lag, notching, bowing, facetting, micro-trenching, profile shape dependence etc. will be discussed.

4:00pm **PS+MM-WeA7 Deep Silicon Etch Profile Control for Micro-Sensor Applications**, ***R.J. Shul***, *M.G. Blain, S.G. Rich, S.A. Zmuda, C.G. Willison, R.P. Manginell*, Sandia National Laboratories

The ability to etch deep, high-aspect ratio, anisotropic, Si features has opened up new areas of application for microelectromechanical systems (MEMS) devices, as well as revolutionized the conception and implementation of "mixed technology" integration. For example, a fully integrated microsystem could include sensors, actuators, electronics, fluidics, and optics in a variety of material systems on a single chip or in a single package. Fabrication of such structures often requires profile control, multi-level etched features, and the ability to form freestanding membrane structures. For example, Si deep reactive ion etch (DRIE) has been used to fabricate a gas chromatographic (GC) separator as part of a micro-chemical analysis system (μChemLab^{TM}) used for the detection of trace concentrations of gas phase analytes. Maintaining uniform, controlled flow dynamics to optimize device performance requires well-controlled etch profiles and smooth etch morphologies. We will report on the use of the DRIE platform to fabricate anisotropic GC columns 100 μm wide, 400 μm deep with 25 μm walls. To improve the separation sensitivity of the GC columns, a new GC design that incorporates 50 μm diameter posts on 80 μm pitch located within 500 μm deep GC columns has recently been fabricated. A new DRIE process was developed to etch these features using parameter ramping, varying reactive gas flow, pressure, and ion energy. The profiles were very anisotropic with smooth features. The use of parameter ramping as well as multi-level masking processes to meet the challenges of advanced micro-sensor designs will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000. .

4:20pm **PS+MM-WeA8 Profile Control as a Function of Process Parameters in Deep Anisotropic Etching of Silicon**, ***M.L. Steen***, *T.J. Dalton*, IBM T.J. Watson Research Center

Deep etching of silicon is integral to the fabrication of microcomponents for microelectromechanical systems (MEMs). New commercially-available etching tools from several manufacturers are capable of deep silicon etching beyond 300 μmm. These systems offer the time multiplexed deep etching (TMDE) technique developed and licensed by Robert Bosch Gmbh, which uses alternating etching and deposition cycles for anisotropic etching of deep silicon structures. During the deposition step, sidewalls are passivated by a polymer deposited from a C_4F_8 discharge. During the subsequent etching cycle flowing only SF_6, both the polymer and silicon are preferentially etched from the base of the trench by ion bombardment. Accurate control of the depth and anisotropy of etched structures is achieved by a fine balance between deposition and subsequent removal of the passivating layer. Processes are well controlled and many types of MEMS devices, such as pressure sensors and accelerometers, are produced using this technology. We are interested in expanding the number and scope of applications using deep silicon etching. Many of these applications have additional demands on surface morphology including minimization of the scalloping observed on vertical sidewalls during TMDE and the roughness of surfaces exposed to the discharge. Moreover, mask undercut and bowing of the etch profiles must be reduced to tailor the slope of etch profiles. Our goal is to understand the evolution of these traits as a function of operating conditions. Toward this goal, a number of process variables were explored using a commercial inductively-coupled plasma etcher. We report a significant increase in the silicon etching rate, minimization of mask undercut, and substantial reduction in bowing. These improvements demonstrate enhanced process performance and flexibility to meet a broad range of needs in deep silicon etching.

4:40pm **PS+MM-WeA9 Mechanisms Involved in the Silicon Cryogenic Etching Process**, ***M. Boufnichel***, GREMI / ST Microelectronics, France, *P. Lefaucheux, R. Dussart*, GREMI, France, *P. Ranson*, GREMI-Universite d'Orleans-CNRS, France

In this study, we investigated the etching and passivation mechanisms involved in the deep cryogenic etching of silicon trenches. More precisely, we studied the dependence of sticking coefficient of oxygen and fluorine as regards to wafer temperature. We showed that fluorine radicals sticking coefficient does not strongly depend on wafer temperature at the contrary to oxygen radicals. XPS measurements allowed us to obtain further informations concerning the nature and behaviour of the passivation layer deposited on trench sides during the cryogenic silicon etching with a SF6/O2 mixture. XPS measurements pointed at the fact that the passivation layer formed during the cryogenic etching of silicon is not mainly composed of SiO2 species. Furthermore, a new method has been employed to determine the effective angular dispersion of ions (EIAD) involved in the etching of silicon and its impact on trench etching evolution. A comparison of the performances of RF and LF bias generators has also been performed so as to highlight the impact of bias-frequency on profile characteristics. A complete study of the etching mechanisms would not have been possible without parallel measurements of physical plasma parameters using Langmuir probe and actinometry with Optical Emission Spectroscopy (OES). The parallel between the etching experiments and diagnostics measurements shows for example that local bowing seems to depend on ion local surface bombardment and passivating mechanisms. Finally, we are able to etch deep anisotropic trenches (100 microns deep and 2 microns in aperture) at a high etch rate, high selectivity (SiO2 mask) and high anisotropy. We performed to reduce or eliminate defects such as local bowing, undercut and notching for different application: etching of HARTs (High Aspect Ratio Trenches), LARTs (Low Aspect Ratio Trenches), vias, SOI (Silicon On Insulator) layers.

5:00pm **PS+MM-WeA10 3-Dimensional Feature Profile Evolution Using Level Set Methods**, ***H. Hwang***, *T.R. Govindan, M. Meyyappan*, NASA Ames Research Center

Modeling feature profile evolution due to etching of semiconductor materials is typically done in two dimensions. However, these 2-D simulations make assumptions about geometries, such as semi-infinite trenches, that are unrealistic. Since a semi-infinite trench will "collect" higher amounts of fluxes than a finite one, the calculated ion and neutral fluxes to the surfaces in 2-D will not account for the shadowing of the opening due to the finite size. These larger fluxes will then lead to a larger overall etch rate, compared with calculations done in 3-D. Furthermore, any asymmetries (due to ion angular distribution functions, for example) can only be captured in 2-D. Inherently 3-D situations, such as striation patterns of the trenches, cannot be studied without the third spatial dimension. We will present results using an etching 3-D simulation which uses level set methods to advance the moving front. This code is an extension of SPELS, the Simulation of Profile Evolution using Level Sets, to calculate etch rates of silicon in chlorine discharges. We will show animations of the evolving trench for different geometries as well as for different process conditions. We will make comparisons of cross sections of the 3-D profiles to calculations from 2-D simulations and demonstrate the effects of a finite trench versus a semi-infinite trench on etch rates.

Plasma Science
Room: C-103 - Session PS+TF-ThM

Plasma Enhanced Deposition
Moderator: T.M. Klein, University of Alabama

8:20am **PS+TF-ThM1 The Correlations between Gas Phase Chemistry, Material Properties, and Device Characteristics of PECVD ZrO_2 Thin Films**, ***B. Cho***, *J.P. Chang*, University of California, Los Angeles

We investigated ZrO_2 as a replacement dielectric film of SiO2 for dynamic random access memory (DRAM) capacitor. We used ECR-PECVD process to deposit ZrO_2 films on p-Si (100) wafers with zirconium tetra-tert-butoxide (ZTB; $Zr(OC_4H_9)_4$) as an organometallic precursor, Ar as a carrier of the precursor vapor, and O_2 as an oxidant. Optical emission spectroscopy (OES), Langmuir probe, and quadrupole mass spectrometry (QMS) were used to characterize the plasma. Using QMS, we identified all oxidation states of Zr and found the compositional abundance shifted from Zr metal and monoxide to Zr dioxide and trioxide with the increase in O_2 /Ar flow rate ratio (O_2 /Ar). Based on the results, we proposed the oxidation and the decomposition reaction mechanisms of ZTB precursors. The as-deposited films obtained without any heating had monoclinic and tetragonal polycrystalline phases based on the grazing incidence x-ray diffraction analysis. High resolution transmission electron microscopy showed that the polycrystalline phase of ZrO_2 was interspersed with amorphous phase and that interfacial layer was formed between the ZrO_2 and the substrate Si. Static secondary ion mass spectrometry showed that Zr concentration was uniform across the bulk ZrO_2 film from both oxygen-rich and oxygen-deficient conditions but Si/Zr ratio was much higher in the interfacial layer obtained in the oxygen-rich condition. This suggested that the oxygen-rich condition resulted in more SiO_2-like interfacial layer. X-ray photoelectron spectroscopy (XPS) showed that stoichiometric ZrO2 film was obtained while an interfacial layer containing Si-O bond was formed even without any O_2 addition to the plasma.

8:40am **PS+TF-ThM2 Low-Temperature Plasma Migration Enhanced Epitaxy of $CuInSe_2$ on GaAs**, ***B.J. Stanbery***, *S. Kincal, S. Kim, T.J. Anderson, O.D. Crisalle*, University of Florida

A comparison of migration-enhanced epitaxial growth[1] of $CuInSe_2$ on GaAs at 350°C with either a thermal cracker or ECR helicon plasma selenium source demonstrates both improved crystallinity and enhanced selenium incorporation using the plasma cracker. Mass spectrometric characterization of the flux from the effusion source coupled to a magnetic-mirror confined 2.45GHz plasma cracker shows 50% enhancement of the Se monomer to dimer flux ratio compared to the thermal double-oven with its cracking zone operating at 1200K, and no measurable ion flux outside the plasma source. Samples grown using the ECR plasma cracker were characterized by a number of differences from all other growth experiments that used the thermal source. The improvement of $CuInSe_2$ epilayer crystallinity is confirmed by the XRD data irrespective of the atomic [Cu]/[In] ratio of the resultant films, which exhibit an order of magnitude reduction in incoherent scattering compared to samples grown with the thermal source, particularly at low angles. Films grown with the plasma source that contain excess copper yield compositions that lie well into the selenium-rich domain of the equilibrium ternary phase field, with little indication of diffraction corresponding to the Cu_2Se binary compound which coexists in equilibrium with $CuInSe_2$ when the overall composition is copper-rich. In contrast, such a peak is always seen in significantly copper-rich layers grown with the thermal source. The higher level of selenium incorporation resulting from MEE growth with the plasma source is discussed in the context of a recent theoretical lattice defect model for $CuInSe_2$ that predicts a significant reduction in the electrical compensation ratio of indium-rich $CuInSe_2$ incorporating a stoichiometric excess of selenium.[2]

[1] Y. Horikoshi, et al., Jap. J. Appl. Phys. 25, L868 (1986).
[2] B.J. Stanbery, Ph.D. Dissertation, U. Fl.(2001).

9:00am **PS+TF-ThM3 2-Dimensional Plasma Simulation of Reactive Physical Vapor Deposition of Metal Nitride**, ***D. Zhang***, *S. Samavedam, J. Schaeffer, R. Martin, P.L.G. Ventzek, P. Tobin*, Motorola Inc.

Reactive physical vapor deposition (RPVD) of metal nitride has been used for interconnect barrier and metal gate deposition due to its relative simplicity in process implementation and lower contamination compared to other deposition techniques requiring chemical precursors. As the electrical properties (e.g. work function, resistivity) of deposited film are sensitive to film characteristics (e.g. composition), optimal process control based on in-depth mechanistic understanding is critical for reactive PVD to meet product requirements. This has motivated our development of a 2-dimensional plasma model for RPVD of metal nitride films. The RPVD model is based on the 2-dimensional Hybrid Plasma Equipment Model (HPEM) developed at the University of Illinois.[1] Plasma is approximated as a fluid in HPEM. A target surface nitridation model (TSNM) has been developed to be self-consistently coupled with HPEM. The TSNM uses a site balance algorithm to address neutral adsorption, desorption by ion sputtering, and surface coverages. An effective sputtering yield for the target is used to account for the effect of target nitridation. The model has been applied to study reactive TiN and Ti_xAl_yN deposition using a parallel-plate PVD tool. It is found that athermal neutrals are the dominant source for deposition. Target nitridation impacts deposition rate by reducing sputtering yield. For Ar and N_2 source gases with a constant total flow, the model derived the dependency of deposition rate with N_2 flow that is in good agreement with experiments. Impact of various process parameters (gas mixture, power, pressure) on deposition characteristics will also be discussed in this work.

[1] P. Subramonium and M. J. Kushner, J. Vac. Sci. Technol. A 20, 325 (2002).

9:20am **PS+TF-ThM4 Expanding Thermal Plasma for SiO_2 Films: A Chemistry-controlled Process and an Insight into the Deposition Mechanism**, ***M. Creatore***, *M. Kilic, K. O'Brien, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO_2 PECVD by means of organosilicon/O_2 mixtures has shown its versatility in many fields, as e.g. IC/MEMS, photonics, optics, mechanics, food packaging. However, some issues concerning the deposition process remain unresolved. For example, the deposition precursors have not been unambiguously identified, hampering a direct correlation between plasma species densities and film composition. The remote expanding thermal plasma (ETP) is introduced as a simplified approach to get insight into the hexamethyldisiloxane (HMDSO)/O_2 deposition process. HMDSO is injected downstream in the expanding argon plasma (generated in a dc cascaded arc) by means of a ring. Because of the expansion, the electron temperature drops to about 0.3 eV: electron-induced dissociations are negligible and the chemical activity is controlled by the (Ar^+, e^-) flow from the arc. The ETP has led to a step-by-step entirely chemistry-controlled process (no ion bombardment) from silicone-like to C-free and dense SiO_2 films, at competitive growth rates (8 nm/s). A multidiagnostics approach has been applied to study the fragmentation and reactions of HMDSO. Cavity Ring Down Spectroscopy (CRD) has been used for OH, CH and CH_3 radicals detection in HMDSO/O_2 plasmas. Together with Mass Spectrometry, CRD has shown that the Si-C bond in the HMDSO molecule appears to break only at very high Ar^+ flux (high arc Ar flow rate and current). Milder conditions favour the Si-O and C-H bond scissions. Films are characterized by means of IR absorption spectroscopy, in situ single wavelength ellipsometry and ex situ spectroscopic ellipsometry. In the presentation the relation between the film properties and the plasma characterization will be addressed.

9:40am **PS+TF-ThM5 Plasma Production of Silicon Clusters and Nanocrystalline Silicon Particles : A New Route for Nanostructured Silicon Thin Films**, ***P. Roca i Cabarrocas***, Ecole Polytechnique, France **INVITED**

The study of silane plasma deposition is important due to the large number of large area devices based on amorphous silicon. When transferring research results to production, deposition rate, uniformity, and powder formation are key issues. In this respect, the study of square-wave modulated discharges revealed that silicon nanocrystals (powder precursors) can be produced even at room temperature. This result has motivated for the work on plasma conditions near the onset of powder formation, to produce better-structured silicon thin films in which silicon clusters, and crystallites formed in the plasma contribute to deposition. Among the nanostructured materials we produced thus far, most work has focused on polymorphous silicon films because they share the high optical absorption of a-Si:H while having improved transport properties. In this presentation we review our recent work on the production, the characterization, and the study of devices based on this new material. The challenging issue of nanoparticle detection in the plasma is addressed with new techniques such as cavity ring down and impedance measurements. Moreover, in situ ellipsometry was used to study the growth and to determine the thermal gradient for which nanoparticles can reach the substrate. In conclusion, the precise control of the size and concentration of nanocrystalline silicon particles in the plasma opens the way to the nanoelectronics field in which the plasma-produced nanocrystallites can be passivated, coated, and incorporated into devices such as non-volatile memories. This is in our opinion an important challenge for the plasma community in the next few years.

10:20am **PS+TF-ThM7 Correlation between Cluster Amount and Qualities of a-Si:H Films for SiH_4 Plasma CVD**, ***K. Koga***, *K. Imabeppu, M. Kai, A. Harikai, M. Shiratani, Y. Watanabe*, Kyushu University, Japan

Recently, clusters below a few nanometers in size formed in SiH_4 high frequency discharges have been pointed out to be a possible cause of light-induced degradation of hydrogenated amorphous silicon (a-Si:H) films. Hence, suppression of cluster growth is an important issue for depositing high quality a-Si:H films at a high rate. To realize such suppression, we have developed a cluster-suppressed plasma CVD method utilizing gas flow and gas temperature gradient.[1] The following results have been obtained in our experiments. 1) Even under so-called device quality conditions, a large amount of clusters (> 10^4 cps) exist in the conventional plasma CVD reactor. 2) Microstructure parameter $R\alpha$ of a-Si:H films decreases with decreasing the cluster amount. The developed cluster-suppressed plasma CVD reactor can decrease both $R\alpha$ and cluster amount below detection limits of our measurement systems ($R\alpha$< 0.003 and cluster amount < 0.001 cps, respectively). These results suggest that a-Si:H films of high qualities can be prepared at a high deposition rate by suppressing the cluster growth. 3) A ratio of cluster amount to deposition rate for a discharge frequency of 60 MHz is 1/20 of that for 13.56 MHz, indicating that the VHF discharge is effective in suppressing cluster growth. 4) Preliminary evaluation of fill factor (FF) of a n^+Si/a-Si:H/Ni Schottky solar cell using a-Si:H films of $R\alpha$= 0.057 shows the high initial value FF_i= 0.57 and high stabilized value after-light soaking FF_a= 0.53, compared to FF_i= 0.51 and FF_a= 0.47 of cell using conventional device quality a-Si:H films of $R\alpha$~ 0.1.

[1] K. Koga, M. Kai, M. Shiratani, Y. Watanabe and N. Shikatani, Jpn. J. Appl. Phys., 41, L168 (2002).

10:40am **PS+TF-ThM8 Plasma and In Situ Film Diagnostic Study of Amorphous and Microcrystalline Silicon Deposition**, ***W.M.M. Kessels***, *J.P.M. Hoefnagels, Y. Barrell, P.J. Van den Oever, M.C.M. Van de Sanden*, Eindhoven University of Technology, The Netherlands

Our comprehensive investigation of the film growth process of amorphous silicon (a-Si:H) from a remote H_2/SiH_4 plasma has recently also been extended to microcrystalline silicon (µc-Si:H). This material is of particular interest for applications in thin film solar cells and thin film transistors because of its higher stability. In this contribution we will compare the absolute densities of the different silane radicals, as determined from cavity ringdown spectroscopy, for the two plasma regimes yielding the two different materials. Moreover, the surface reaction probability of the silane radicals will be presented as obtained under real deposition conditions (e.g., as a function of substrate temperature) by time-resolved cavity ringdown experiments. >From this information, it is, for example, revealed that Si, SiH, and SiH_3 radicals have approximately an equal contribution to µc-Si:H growth, unlike a-Si:H film growth which is almost completely governed by SiH_3. Furthermore, we will present 'film depth-information' with respect to hydrogen bonding, hydrogen concentration, and other structural film properties as has been obtained by in situ monitoring of film growth by attenuated total reflection infrared spectroscopy and spectroscopic ellipsometry. This powerful combination of diagnostics applied to the well-characterized plasma conditions has revealed a rather homogeneous hydrogen distribution throughout the film (also for µc-Si:H) apart from an initial incubation phase corresponding to interface/surface layer formation. The interface thickness and surface roughness increase with increasing deposition rate but decrease with increasing substrate temperature. New insights into the film growth process of both materials will be discussed.

11:00am **PS+TF-ThM9 Mechanism of Hydrogen-Induced Crystallization of Amorphous Silicon Thin Films**, ***S. Sriraman***, *E.S. Aydil, D. Maroudas*, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) films are used in solar cells, displays, and imaging devices. The a-Si:H films undergo chemically-induced structural transformation from a state of disorder to order (crystallinity) when exposed to H atoms from an H_2 plasma at temperatures lower than those required for thermal annealing; exposure to an H_2 plasma is used as a post-deposition treatment step for plasma-deposited a-Si:H films. In addition, nc-Si:H films can be grown during plasma deposition by heavily diluting the SiH_4 feed gas with H_2. Though several hypotheses have been proposed, the mechanism behind the H-induced disorder to order transition still remains unclear. The atomic-scale processes behind this structural transition are analyzed through molecular-dynamics (MD) simulations of repeated H atom impingement on a-Si:H films. These films were grown through MD by repeatedly impinging SiH_3 radicals on an initially H-terminated Si(001)-(2x1) surface. The evolution of the Si-Si radial distribution function during H exposure of the film showed gradual appearance of peaks corresponding to the coordination shells of crystalline Si, indicating a transition from disorder to order. Detailed structural analysis after H exposure revealed the presence of a nanocrystalline region embedded within the amorphous Si matrix. The structural transformation is mediated by H atoms that diffuse into the a-Si:H film and insert into strained Si-Si bonds to form intermediate bond-centered H (Si-H-Si) configurations. This results in local structural relaxation of these strained Si-Si bonds. The energetics of H insertion into strained Si-Si bonds and its implications in the structural relaxation of the amorphous phase are discussed. The existence of bond-centered H(D) in a-Si:H films exposed to H(D) atoms from a $H_2(D_2)$ plasma also was verified experimentally through in situ infrared spectroscopy.

11:20am **PS+TF-ThM10 On the Roughness Evolution during Remote PECVD of Amorphous Silicon**, *M.C.M. Van de Sanden*, ***A.H.M. Smets***, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

The roughness evolution during the growth of hydrogenated amorphous silicon is studied in situ by means of single wavelength ellipsometry. The roughness measurements are corroborated by ex situ spectroscopic ellipsometry and Atomic Force Microscopy on films having thickness in the range from 30 up to 3000 nm. The films were deposited by means of the expanding thermal plasma, a remote plasma technique. Silane is injected downstream in an Ar/H_2 plasma. From detailed measurements in the gas phase it is established that the dominant radical contributing to the film growth is the silyl radical with minor contributions from other radicals such as Si, SiH and H. The self-bias is small which characterizes the a-Si:H growth from this dominantly SiH_3 source as purely chemical in origin. The roughness evolution is analysed by means of the scaling properties of the surface as first proposed by Family and Vicsek.[1] It is found that the surface width scales with film thickness d as d^{β}. β, the dynamic scaling exponent, is determined as function of substrate temperature and growth rate. A cross-over from random deposition (β = 1/2) at low substrate temperatures, to a deposition process in which surface diffusion dominates the roughness evolution is observed. The scaling universality class of the roughness development of the growth of a-Si:H shows great similarity with, e.g., Molecular Beam Epitaxy of crystalline silicon. The activation energy from beta vs. substrate temperature is determined from comparing the data with a solid-on-solid model and is about 1 eV. This value is much higher than expected on basis of the conventional growth models for a-Si:H, in which the weakly adsorbed SiH_3 radical is assumed to rule the roughness evolution. The implications for the growth model of a-Si:H will be discussed.

[1] F. Family and T. Vicsek, J. Phys. A 18 L75 (1985).

11:40am **PS+TF-ThM11 Detailed Study of Chemistry of Ar/C_2H_2 Plasma and Consequences For the a-C:H Film Growth**, *J. Benedikt, R.V. Woen*, ***M.C.M. Van de Sanden***, Eindhoven University of Technology, The Netherlands

The role of hydrocarbon radicals during the deposition of a-C:H films is studied in an Ar/C_2H_2 remote expanding thermal plasma (ETP) reactor. C, C_2 and CH radicals are detected by means of cavity ring down spectroscopy (CRDS) at different plasma conditions and at different positions downstream from the thermal plasma source. A broadband absorption (BBA) is observed in the 250 - 520 nm region. Acetylene and diacetylene (C_4H_2) are monitored with a residual gas analyser. A simple plasma chemistry model is developed to explain measured data. The plasma chemistry is governed by argon ion induced dissociation of acetylene molecules. Main product of this reaction is the ethynyl (C_2H) radical, which can further react either with argon ions or with acetylene, depending on the ratio between the flux of argon ions and the flux of acetylene into the reactor. The BBA is due at least two species: most likely candidates are C_2H radical and C_4H_2 molecule. In-situ real-time ellipsometry was used to determine growth rate and refractive index of the films grown. Our preliminary conclusion is that C_2H radical is a growth precursor for high quality hard diamond-like a-C:H films; a-C:H films with slightly lower hardness but faster growth rate were also deposited using a C_4H_2 rich plasma. The loss probabilities of the ethynyl radical and diacetylene molecule are determined from time dependent CRDS. The probabilities can be used to monitor the relative importance of the ethynyl radical vs. diacetylene in the growth of a-C:H.

Plasma Science
Room: C-103 - Session PS-ThA

Dielectric Etch II

Moderator: A.P. Mahorowala, IBM T. J. Watson Research Center

2:00pm **PS-ThA1 Etching Reaction Mechanism of Organic Low-k Dielectric Employing High-Density Plasmas and Multi-Beams**, ***M. Hori***, *H. Nagai*, Nagoya University, Japan, *M. Hiramatsu*, Meijo University, Japan, *T. Goto*, Nagoya University, Japan

An organic film, FLARE, is one of the most prospective candidates for interlayer insulating films with lower dielectric constant (low-k). N_2/H_2 and N_2/NH_3 gas plasmas have been used for etching organic low-k film without degrading the film quality and etch profile. The organic low-k film etching has been studied in ultrahigh frequency (UHF) plasma and inductively coupled plasma (ICP) employing N_2/H_2 and N_2/NH_3 gases. The absolute densities of H and N radicals were measured using the vacuum ultraviolet absorption spectroscopy (VUVAS) employing micro-plasma as a light source. N and H radical densities were estimated on the order of 10^{11} - 10^{12} cm^{-3} and 10^{12} - 10^{13} cm^{-3}, respectively. The behavior of etch rate corresponded to that of H radical density. Therefore, H radicals were found to be important species for organic low-k film etching, while N radicals never etched without ion bombardments. To investigate the roles of radicals and ions from view point of fundamental reactions, the organic low-k film etching reaction was investigated using radical and ion beams. H and N radicals ($\geq 10^{10}$ cm^{-3}) were injected with changing the density under the irradiation of each ion (Ar^+, N_2^+, NH_4^+, H_3^+) with an energy of 500 eV. The etch rate of organic low-k film was linearly increased with increasing H radical density, while suppressed drastically by N radical injection. The etched subsurface reactions of radicals were investigated by in-situ X-ray photoelectron spectroscopy (XPS) and fourier transform-infrared attenuated total reflection (FT-IR ATR). The etching reaction mechanism is discussed on the basis of results in plasma and multi-beam etching.

2:20pm **PS-ThA2 Modeling Dual Inlaid Feature Construction**, ***P.J. Stout***, *S. Rauf, T. Sparks, D. Zhang, P.L.G. Ventzek*, Motorola

A reactor/feature physics based modeling suite has been applied to dual inlaid (DI) via first trench last (VFTL) feature construction. The reactor model is HPEM (developed at the University of Illinois) and the feature model is Papaya (developed at Motorola). Papaya, a 2D/3D Monte Carlo based feature scale model, includes physical effects of transport to surface, specular and diffusive reflection from surface, adsorption, surface diffusion, deposition, sputtering, etching, and crystal structure. Papaya is coupled to the reactor model through "atomic sources". The atomic sources are the identity, flux rate, angular distribution, and energy distribution of specie incident on the feature surface. The atomic sources are used by the feature model to predict feature evolution. The DI feature is used in inlaid copper interconnect construction to define metal lines and their connection to the metal layer below. The advantage of the DI feature is only one metallization step (barrier/seed/plating/CMP) is required to deposit metal into both the metal lines and the via connections to the metal layer below. The DI feature is constructed through a combination of etch, fill, and mask steps. Discussed will be the 3D feature modeling of flurocarbon plasma etching of vias and trenches in SiO_2 to construct a VFTL DI feature. The significant feature effects have been simulated for the interaction of trench etch and etched via profile and the via protect fill material. Effects of feature geometry, via protect material level, and polymerization thickness on the final 3D DI feature profile will be discussed.

2:40pm **PS-ThA3 Profile Evolution During Fluorocarbon Plasma Etching of Low-k Porous Silica**[1], ***A. Sankaran***, *M.J. Kushner*, University of Illinois at Urbana-Champaign

To achieve shorter RC-delay times in integrated circuits low-k dielectric materials are being investigated for interconnect wiring. Porous silica is a promising candidate. Profile evolution and maintenance of critical dimensions during plasma etching of porous silica are problematic due to the exposure of open pores. To investigate these issues, reaction mechanisms for fluorocarbon plasma etching of porous silicon-dioxide have been developed and incorporated into the Monte-Carlo Feature Profile Model (MCFPM) which was modified to address these two-phase systems. To focus on issues related to the morphology of porous materials, the porous silica in the model was treated as stoichiometric SiO_2. Pores are randomly distributed in the SiO_2 to have a specified average pore radius and volume fraction (porosity). Fluxes to the substrate were obtained from the Hybrid Plasma Equipment Model for inductively coupled plasmas sustained in CHF_3, C_2F_6 and C_4F_8. The surface reaction mechanisms for these chemistries were validated by comparison to experiments.[2] Etch rates and tapering of high aspect ratio features were investigated as a function of bias voltage and diluents (e.g., Ar). We found that etch rates for porous silica materials are generally higher than for SiO_2 even when accounting for the smaller mass density, though etch rates do not necessarily scale linearly pore size or porosity. Scaling parameters (e.g., more tapering with larger polymerizing fluxes) observed for solid SiO_2 are generally applicable to the porous materials. Removal of polymer from exposed pores was also investigated using O_2 plasmas.

[1]Work supported by Semiconductor Research Corp. and National Science Foundation.
[2]Oehrlein et al. JVST A 17, 26 (1999); 18, 2742 (2000)

3:00pm **PS-ThA4 The Effect of Aspect Ratio on the Etching Properties of Porous Low-k Material in Fluorocarbon Plasma**, *S.H. Moon*, ***S.-W. Hwang***, *G.-R. Lee, J.-H. Min*, Seoul National University, Korea

As the critical dimension of integrated circuit devices rapidly shrinks to sub 0.1μm range, micro-structures such as trench, contact and via holes have high aspect ratios and consequently the issue of the aspect-ratio-dependent-etching (ARDE) becomes important. In ARDE study, information about the surface properties of the sidewall and the bottom inside the features is important, but there are few studies about this, especially in low-k interlayer dielectric etching, because the direct analysis of the surface in real features is difficult. In this study, we used a Faraday cage, which allowed us to control the ion incident angle on the substrate, and investigated in macroscopic scale the change in the roughness and chemical composition of porous low-k silsesquioxane with the aspect ratio of trench-shaped structure after etching in CF_4 and CHF_3 plasmas. For the etching experiments, we placed trench structures made of porous silsesquioxane inside the Faraday cage, and the samples were processed at 4mTorr, 600W source power, and -100V bias voltage in TCP etcher. The sidewall height of the samples was fixed at 1cm and the bottom width was varied between 1mm and 1cm such that the aspect ratio of the trench structure was varied between 10 and 1. Etch rates of the bottom and the sidewall of the samples for different aspect ratios were correlated with their surface properties observed by AFM, AES, and FT-IR.

3:20pm **PS-ThA5 Etching of Porous Low-K Dielectric Films in Fluorocarbon Plasmas**, ***S.A. Rasgon***, *B.E. Goodlin, H.H. Sawin*, Massaschusetts Institute of Technology

To further reduce interconnect delay and enable higher device speeds (especially as the critical dimensions are lowered below 0.13 μm), it becomes advantageous to reduce the dielectric constant of the interlevel dielectric material between the metal lines. Porous low-k materials are potential candidates to meet this objective. While current research has focused on the material characterization of porous low-k films, little attention has been paid to the etching characteristics, of critical importance for process integration. Our research focuses on the etching characteristics and kinetics of leading candidate porous low-k dielectric films in fluorocarbon chemistries. Etching characteristics of these films are simultaneously compared with OSG, SiO_2, SiC(N), and photoresist films to reveal similarities and differences in etching behavior, and selectivity toward mask and stop layers. Ellipsometric results on porous low-k films indicate a possible competition between diffusion of etching precursors into the porous matrix, and ion-enhanced etching. Specifically, at low DC bias voltages, we note what appears to be a mixed fluorocarbon/porous-low k layer, possibly several hundred Å deep. As DC bias is increased, the mixed layer thins, and disappears around 300 V DC bias. This mixed layer is not present on OSG or SiO_2 samples etched at the same conditions. XPS studies will confirm these results. Understanding these etching behaviors may provide valuable insight into solving the problems of damage to the dielectric constant of porous low-k films, and reverse - selectivity during etching of the stop layer.

3:40pm **PS-ThA6 Plasma Etching Chemistry and Kinetics for Low-k and Porous Low-k Dielectric Films**, ***W. Jin***, Massachusetts Institute of Technology

To further reduce interconnect delay and enable higher device speeds, especially as the critical dimensions are lowered below 0.13μm, the interlevel metal insulator material with dielectric constant as low as 2.0 is desired. Porous materials, which lower the dielectric constant as a result of mixing air with the solid phase, are potential candidates to meet the low dielectric constant objective. Current research is focused on the material characterization, but little attention has been paid to its etching

characteristics, although they are critical for process integration. In this research, we have measured etching rates of both porous low-k and low-k (OSG) as functions of ion bombardment energy, ion impinging angle with various fluorocarbon plasma beams, which are necessary for profile evolution modeling of porous low-k etching in inductively coupled plasma. In this work, ions and neutrals are extracted directly from plasma to the main chamber evacuated by a cryo-pump. Surface reaction is studied by measuring etching rate with an ex-situ spectroscopic ellipsometer. At the same time, ion and neutral composition of the plasma is determined with mass spectrometer. And surface composition is analyzed by an X-ray photoelectron spectroscopy. The possible reasons attributing to the difference of the etching behavior between porous low-k and low-k dielectric films has been studied.

4:00pm **PS-ThA7 In Situ Real Time Monitoring of Evaporation Induced Self-Assembly and Patterned Etching of Low-k Mesoporous SiO_2 in Fluorocarbon Plasmas**, *H. Gerung, C.J. Brinker,* ***S. Han***, University of New Mexico

We have investigated in situ and in real time the sol condensation and the plasma-assisted patterning of mesoporous low-k SiO_2 films, using attenuated total reflection Fourier transform infrared spectroscopy. The porous SiO_2 films are prepared by evaporation induced self-assembly (EISA). The evaporation of ethanol in the sol induces self-assembly of surfactants to form an ordered cubic-phase template. Around this template, tetraethylorthosilicate (TEOS) condenses to create a silica network. The template is subsequently removed by calcination, resulting in a cubic phase mesoporous SiO_2 film. To better understand the condensation sequence, we have monitored the dichroic ratio of Si-O-Si IR absorbance during EISA and examined the propagation of Si-O-Si bond formation for varying film thicknesses. Thus formed porous SiO_2 films, stacked with a patterned photoresist, are etched in an inductively coupled plasma reactor, using CHF_3 and Ar. During etching, the integrated IR absorbance by Si-O-Si asymmetric stretching modes near 1080 cm^{-1} decreases while that of C-F_x (x = 1, 2, or 3) stretching modes near 1300 cm^{-1} continues to increase. The rate of decrease in integrated Si-O-Si absorbance translates to the SiO_2 removal rate. When corrected for the exponentially decaying evanescent electric field, the removal rate helps monitor the evolution of the etch profile in real time. We attribute the increasing integrated absorbance to the formation of C-F_x species along the sidewall of patterned SiO_2 trenches. The stretching vibrational modes of carbon-carbon double bonds (C=C) are not observed near 1700 cm^{-1}. The absence of C=C absorbance with the presence of C-F_x absorbance indicates that the sidewall passivation maintains a steady state thickness. We intend to exploit the SiO_2 removal rate and the observed nature of sidewall passivation to predict the etch profile.

4:20pm **PS-ThA8 The Control of the Etching of SiOCH Films using C_4F_8/Ar/N_2 Plasma**, ***T. Tatsumi***, Sony Corporation, Japan, *K. Urata,* Sony Computer Entertainment, Japan, *K. Nagahata,* Sony Corporation, Japan, *S. Iseda,* Sony Computer Entertainment, Japan, *Y. Morita*, Sony Corporation, Japan

The relationship between the etch rates, C-F polymer thickness and the incident fluxes in dual-frequency (60/2MHz) RIE was evaluated by using various in-situ measurements tools, such as IRLAS and OES. To vary the amount of incident CF_x species, the C_4F_8 partial pressures in the C_4F_8/Ar/N_2 (or O_2) was increased under a gas pressure of 75 mTorr and a V_{pp} of 2000 V. The C-F polymer thickness increased when the incident CF_x fluxes were relatively higher than the removal ability of the C-F polymer; that mostly depends on the O and N fluxes (including the O outflux from etched SiOCH). SiOCH films have some methyl groups in the Si-O network and their densities are lower than SiO_2. Comparing to SiO_2 etching, the outflux of O decreased while additional C from the etched surface of SiOCH was supplied to the C-F polymer layer. The difference in outfluxes between SiO_2 and SiOCH drastically changed the process window for the selective etching. We found that the optimum etching condition could be obtained below the "critical point" P_c, where the total C flux became equivalent to O and N total fluxes. We have to carefully control the partial pressure and dissociation degree of C_4F_8 according to the density, composition and aspect ratio of the SiOCH sample and thus find the P_c at witch the maximum etch rate can be obtained. This is because the process window is very narrow and slight change in radical fluxes can induce phenomena such as residues and etch stop that cause serious problems with etching performance.

[1]T.Tatsumi et al., Proceedings of 22nd Symposium on Dry Process (2000) 37.

4:40pm **PS-ThA9 SiO_2 Etch Lag in SiO_2/SiLK™/SiO_2 Stack Structures**, ***A. Hasegawa***, *K. Ohira, T. Mizutani,* Fujitsu Limited, Japan, *K. Higuchi,* Fujitsu Vlsi Limited, Japan, *M. Okamoto, M. Nakaishi, K. Nakagawa,* Fujitsu Limited, Japan

The etching of stack structure using hard-mask became indispensability by the adoption of the dual damascene process and organic low dielectric constant (k) material for Cu wiring. In this study, SiO_2 etch lag effect depending on existence of SiLK™ layer in stack structure is investigated. SiLK™ is low-k organic dielectrics considered as perspective candidates for the use in microelectronic industry. The sample used in this experiment consists of SiN/upper SiO_2/SiLK™/lower SiO_2 stacked structure. SiN was used for hard-mask to etch SiO_2. Upper SiO_2 was used for cover layer to protect SiLK™ damage during ashing and/or planarization by chemical mechanical polishing. After SiN trench etch, SiN/upper SiO_2/SiLK™ were etched using hole patterned photoresist mask. Photoresist mask was removed during SiLK™ etch. Then, trench pattern of upper SiO_2 and via pattern of lower SiO_2 were etched at the same time using the patterned SiN/upper SiO_2/SiLK™ layers. The etching of the upper and lower SiO_2 were performed in commercial UHF plasma reactors using a C_5F_8/Ar/O_2 chemistry. The lower SiO_2 etch depth was measured from cross-sectional-scanning-electron-microscopy (SEM) photographs. The etch rate of dense via was 284nm/min. On the other hand, in the isolated via, the etch rate was only 91nm/min. However, in the case of using the stack sample, which was replaced SiLK™ with SiN, etch rate of dense and isolated via were equivalent at 282nm/min. It was found that existence of SiLK™ decreases the SiO_2 etch rate of a particular via pattern remarkably.

5:00pm **PS-ThA10 Etch Process Development of Porous Low-k Dielectrics for Dual Damascene Copper Interconnects**, ***K.D. Brennan***, Texas Instruments, *J.M. Jacobs,* Philips, *P.J. Wolf,* Intel

Advances in plasma etch technology are necessary to integrate low-k dielectrics and low-resistance metal leads to reduce interconnect RC time delay in order to meet the requirements of the Intemational Technology Roadmap for Semiconductors (ITRS). International SEMATECH (ISMT) is currently implementing dual damascene copper interconnects built with porous low-k dielectrics as a means to meet future interconnect requirements. Development and optimization of an etch process for JSR LKD 5109, a porous methyl-silsesquioxane (pMSQ) based dielectric with a k-value of 2.2 is presented. Two level metal interconnects are fabricated, using a dual hard mask approach. The advantages and limitations of this approach for the etch process are discussed.

Plasma Science
Room: C-103 - Session PS-FrM

Plasma Surface Interactions II

Moderator: W.M.M. Kessels, Eindhoven University of Technology

8:20am **PS-FrM1 Study of SiO_2 Etching with Plasma-beam Irradiation**, ***K. Kurihara***, *A. Egami, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for $Si/SiO_2/SiN$ etching to achieve high etching performance. A study of the SiO_2 etching mechanism has been still needed to construct a process simulator without experiments of trial and error. A plasma-beam irradiation apparatus, which can control plasma parameters, such as ion energy and radical/ion composition, is very useful to examine the plasma-surface interactions under a real etching environment. We measured Si containing desorbed products from the SiO_2 substrate by quadrupole mass spectrometer during $^{13}CF_4/Ar$ gas mixture plasma beam irradiation. Furthermore we analyzed a surface reaction layer by a quasi-in situ X-ray photoelectron spectroscopy analysis after the plasma-beam irradiation. Composition of the desorbed products was almost independent on the ion energy under the condition that the ratio of the radical flux to the ion flux was small (1~2:1). Major desorbed products were SiF_2 and SiF_4. The thickness of the surface reaction layer including Si-F bond increased with increase in the ion energy, but bonding state in the reaction layer did not change. At the relatively high ion energy above 500 eV and ion rich condition, ions play an important role in etching. On the other hand, under the condition that the ion energy was low (~300eV) and the ratio of the radical flux to the ion flux was about 10:1, the relative ratio of highly fluorinated species (SiF_4) increased slightly. Radical species may affect the production of desorbed products at the low ion energy. We will discuss mechanisms of selective etching of SiO_2 to Si or SiN under these conditions, which leads the achievement of the high selectivity for sub-100nm LSI circuit production. This work was funded by NEDO.

8:40am **PS-FrM2 Measurements of Desorbed Products and Etching Yield by CFx+(x=1,2,3) Ion Irradiation**, ***K. Karahashi***, *K. Ishikawa, H. Tuboi, K. Yanai, K. Kurihara, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon plasma has been widely used to etch silicon dioxide in the fabrication of semiconductor devices. For further development of integrated semiconductor devices, more precise control of the etching process is required. Thus, we have developed a mass-analyzed ion beam apparatus; Energy controlled single species ions are irradiated to SiO2 surface under ultra-high vacuum condition, and we can study the roles of individual fluorocarbon ion irradiation without gas phase reactions or neutral radicals irradiation. In the present work, we have investigated desorption products and etching yields for silicon or silicon dioxide by CFx+ (x = 1-3) ion bombardments. Desorbed products could detected with a quadrupole mass spectrometer by pulse ion beam method, and estimate the kinetic energy of desorbed products from the time delay of waveform from incident ion pulse. In SiO2 etching by CFx+ ion irradiation, the major desorbed product, which contains silicon, was SiF2. The kinetic energy of SiF2 was less than 0.1 eV. Therefore, products were different from physical sputtering particles such Si and SiF as desorbed from silicon surfaces by CFx+ (x = 1-3) ion bombardments. Etching yields for SiO2 were measured as a function of incident ion energy. The etching yield by F+ ion was smaller than that of Ar+ ion. The effect of chemical reaction of F+ ion did not clearly appeared. Etching yields of CFx+ (x = 1-3) increased with increasing the ion energy and with increasing number of fluorine atom in the ions. Above 1000 eV, etching yields is gradually saturated. Below 500 eV, etching yields abruptly dropped with decreasing ion energy, and fluorocarbon films grew on surfaces. These results suggest that the etching reaction is affected by chemical reactivity of the incident ions, and that the etching reactions are controlled by the incident ion energy and species. This work was supported by NEDO.

9:00am **PS-FrM3 Etch Mechanisms of SiOC and Selectivity to SiO_2 and SiC in Fluorocarbon Based Plasmas**, ***N. Posseme***, *T. Chevolleau, L. Vallier, O. Joubert*, CNRS/LTM, France, *P. Mangiagalli*, Applied Materials, France

In CMOS technology, the traditional SiO_2 is being replaced by the so called low k materials in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. Many inorganic materials such as doped oxide and organic materials are being investigated as potential candidates. In this work, the study is focused on the etching of two carbon doped oxide materials: SiOC (k = 2.9) and porous SiOC (k=2.2 with a porosity of 40%). With these new inorganic materials, fluorocarbon-based etch processes have to be revisited to obtain adequate profile control in high aspect ratio structures, high etch rate and good selectivities to etch stop or hard mask such as SiO_2 (k = 3.9) and SiC (k = 4). This study is dedicated to an analysis of the etch mechanisms of SiOC, SiO_2 and SiC in fluorocarbon plasmas. The etching of these materials is carried out on blanket wafers in a MERIE reactor (Magnetically Enhanced Reactive Ion Etcher) using different fluorocarbon gas (CF_4, C_4F_6, CH_2F_2) mixed with Ar, O_2 and N_2. X-ray Photoelectron Spectroscopy (XPS) analysis of the surface after partial etching shows that the fluorocarbon layer thickness formed at the surface plays a key role in controlling the etch rate and selectivity of SiOC, SiO_2 and SiC. The XPS results indicate that the fluorocarbon layer thickness depends on the plasma chemistry and also on the oxygen and carbon concentration in the etched materials The polymerising gas addition such as CH_2F_2 to $CF_4/N_2/Ar$ gas mixture induces an increase in thickness of the fluorocarbon layer which generates a decrease in etch rate. Similar XPS analysis are also conducted on the SiOC sidewalls using the chemical topography analysis technique.

9:20am **PS-FrM4 Hydrophilic Plasma Surface Modification of Membranes: Surface Analysis, Gas-Phase Diagnostics, and Mechanisms of Energy Transfer**, ***K.R. Kull***, *J. Zhang, E.R. Fisher*, Colorado State University

Treatments with nitrogen containing plasma that render asymmetric polyethersulfone (PES) membranes permanently hydrophilic are reported. The modification strategy entails treating these membranes downstream from an inductively coupled rf plasma source. Contact angle measurements confirm that the membranes are wettable as a result of treatment with plasmas containing nitrogen species (Ar/NH_3, O_2/NH_3, N_2). More importantly, the hydrophilic modification is permanent as plasma-treated membranes remain wettable for more than eight months after plasma treatment. The change in wettability is a result of chemical changes in the membrane induced by plasma treatment. FTIR and XPS analysis of treated membranes reveals the incorporation of nitrogen functionalities into the treated membranes. Moreover, there is a concomitant increase in the oxygen to carbon ratio compared to the untreated PES membrane. Mass spectral data reveals gas-phase species are created from plasma-membrane interactions and SEM investigations reveal no visually observable structural damage as a result of the treatment parameters employed. We have also investigated the role of NH and NH_2 radicals in the modification process using laser-induced fluorescence measurements. The velocity of NH radicals in the nitrogen-containing plasmas has been measured and appears to be rf power dependent. Additional data on the surface interactions of NH with PES membranes as well as velocity measurements for scattered NH radicals will be presented and compared to earlier results for NH_2 radicals.[1] Implications for plasma modification mechanisms will also be discussed.

[1]C. I. Butoi, M. L. Steen, J. R. D. Peers, E. R. Fisher, J. Phys. Chem. B 105, 2001, 5957.

9:40am **PS-FrM5 Radical Reactions with Organic/Polymeric Surfaces**, ***J. Torres***, *C.C. Perry, S. Bransfield, D.H. Fairbrother*, Johns Hopkins University

Plasmas play an important role in polymer surface modification based on their ability to introduce new functionalities at the interface. Atomic or molecular radicals are often cited as the key species responsible for initiating surface reactions during plasma processing. Due to the wide range of reactive species within a plasma, however, surface reactions of individual species are hard to determine. In our work we report the results of the reactions of O and Cl radicals generated by thermal dissociation of O_2 and Cl_2 respectively, with organic thin films and polymers. The present study focuses on the interaction of atomic and molecular oxygen and chlorine with an X-ray modified hexadecane thiols adsorbed on gold using in situ XPS. Oxygen reaction with these hydrocarbon films proceeds in three stages. Initially the reaction dynamics are dominated by the incorporation of new oxygen containing functionalities at the vacuum/film interface. At intermediate O/O_2 exposures, when a steady state concentration of C-O, C=O and O-C=O groups has been established, the production of volatile carbon containing species, including CO_2 is responsible for etching the hydrocarbon film. Upon prolonged O/O_2 exposures, O atoms penetrate to the film/substrate interface, producing Au_2O_3 and sulfonate (RSO_3) species. In contrast, chlorine radicals do not etch the hydrocarbon surface and produce a uniform distribution of CCl and CCl_2 species in the near surface region. The advantages of employing self-assembled monolayers as models for polymeric interfaces as well as the interaction of oxygen and chlorine

radicals with polyethylene characterized by XPS, ATR-IR and AFM will also be presented.

10:00am **PS-FrM6 The Interaction Dynamics of Ar/H Plasmas with Silicon Surfaces**, *J. Villette, F. Gou,* ***M.A. Gleeson****, A.W. Kleyn*, Leiden University, The Netherlands

Despite its technological importance the basic reaction dynamics of plasma deposition and etching processes are not known, even though in this case the process takes place almost under vacuum and should be easily accessible to studies at the molecular level. We have developed a new machine for such studies. Samples are placed in the centre of a 70 cm diameter reaction chamber, which can be evacuated up to ultra high vacuum. A cascaded arc plasma source produces an atmospheric plasma, which is collimated and differentially pumped. With a quadrupole mass spectrometer (QMS) we can monitor the particles emitted. An ion beam is produced in an independent source and can be scattered from the crystal that is being modified by the plasma. A time and position sensitive detector (PSD) records the scattered ions and neutrals individually. From their energy and scattering pattern we reconstruct the actual state of the surface. In order to prepare and characterize samples we can remove them from the reaction chamber into the preparation chamber under vacuum. Scattering of protons from clean and hydrogen covered silicon has been studied extensively by Souda et al.[1] The protons reflection is very sensitive to the state of the surface. In our machine we apply this to hydrogen treatment of Si(110). We note that the reflected yield goes up dramatically when switching on the hydrogen discharge. Switching to an Ar discharge we observe the disappearance of the strong hydrogen signal, indicating that even hyperthermal Ar from a cascaded arc recombining plasma is capable of removing hydrogen from silicon.

[1] R. Souda, E. Asari, T. Suzuki, and K. Yamamoto, Surf. Sci. 431, 26 (1999).

10:20am **PS-FrM7 Electron-Stimulated Atomic Scale Recovery of Ion-Induced Damage on Si(100)**, ***T. Narushima***, NRI-AIST, Japan, *M. Kitajima*, NIMS, Japan, *K. Miki*, NRI-AIST and NIMS, Japan

Recently, an importance of process under plasma irradiation is getting higher, because of its high reactivity and reducing process temperature. Surface damages induced by the plasma can be troubles for subsequent processes. But, effects of the plasma irradiation on the damage with atomic level have not been well studied. Previously, we reported that low energy (<40eV) electrons may be used to athermally release the compressive stress in the Si(001) surface layer induced by Ar^+ ions (<100eV) with using the ion and electron accelerated from Ar plasma [Narushima et al., Appl. Phys. Lett. 79, 605 (2001)]. In particular, we have strong evidence that the stress relaxation was found to depend only on the number of irradiated electrons and was independent of the total energy deposition. This indicates that complete relaxation is not promoted by a thermal activation mechanism, but by a non-thermal mechanism. In this paper, we show using scanning tunneling microscope (STM) that the underlying cause of the surface stress relaxation is athermal recrystallization of the surface atoms. Our finding is opposite to the previous report by Nakayama et al. [Phys. Rev. Lett. 82, 980 (1999)] that energetic electrons (>90eV) induce atomic scale damage. This discrepancy may be explained if we delineate 40-90 eV (in the case of Si) as the threshold between thermal and athermal processes for electron-surface atoms interactions. Our STM observation shows chracteristic features to support our hypothesis. The ion-bombarded surface does not have the thermally-generated 2x1 surface reconstruction, but instead a 1x1 reconstruction, which is slightly closer to positions of a 'bulk terminated' surface.

11:00am **PS-FrM9 Reduction of Hole Currents and E' centers in SiO_2 Induced by Vacuum-Ultraviolet-Light Using Pulse-Time-Modulated Plasma**, ***Y. Ishikawa***, *M. Okigawa, S. Kumagai, S. Samukawa*, Tohoku University, Japan

Plasma processes have been widely used in the fabrication of MOS-LSIs. Some vacuum-ultraviolet lights (VUV) in the plasma generates electron-hole pairs in SiO_2 because of its higher energy than the SiO_2-band-gap. The holes are trapped in SiO_2 and interface states are often formed at the SiO_2-Si boundary.[1] We have reported that pulse-time-modulated (TM) plasma reduce the VUV in the plasma and the hole current in SiO_2.[2] In this study, to understand the relationship between the hole current and damages in SiO_2, the hole current and E' centers (trapped electron at oxygen vacancy in SiO_2) are measured by on-wafer-monitoring and electron-spin-resonance technique (ESR). An aluminum film was deposited on SiO_2 of the on-wafer-monitoring device to eliminate charged particles from the plasma. The more the hole current, the more E' centers were observed in the on-wafer-monitoring device when the TM-He-plasma condition were varied. We also evaluated the time-resolved measurement of the electron density and the VUV intensity in the TM plasma. The VUV light intensity and the hole current decayed just after the plasma-off in TM plasma, whereas the electron density declined with four times longer decay constant. These results indicate that the TM plasma reduce an increase in E' centers as damages due to decrease in the hole current resulting from suppression of the VUV. Additionally, we appraised a depth profile of E' center, resulting in gradually decline and reaching nearly zero at a depth of 15 nm. The relationship between a VUV penetration depth and the E' center profile will be discussed in the meeting.

[1]D. V. McCughan and V. T. Murphy: J. Appl. Phys. 44 (1973) 2008, T. Yunogami, T. Mizutani, K. Suzuki and S. Nishimatsu: Jpn. J. Appl. Phys., 28 (1989) 2172

[2] S. Samukawa, Y. Ishikawa, S. Kumagai and M. Okigawa: Jpn. J. Appl. Phys., 40 (2001) L1346.

11:20am **PS-FrM10 Evolution of Line Edge Roughness During Poly-Si Gate Stack Etching**, ***S. Rauf***, *P.J. Stout, J. Cobb*, Motorola Semiconductor Products Sector

As the transistor dimensions in integrated circuits continue to shrink, the influence of gate surface roughness on transistor electrical characteristics is expected to grow. As a consequence, there is considerable need for gate fabrication processes that minimize or mitigate photoresist and poly-Si gate surface roughness. An integrated 2-dimensional (2D) plasma equipment - feature evolution model has been used to study roughness evolution on photoresist and poly-Si gate surfaces during gate stack etching. The model considers a sequence of typical gate etch processes including resist trimming, anti-reflective coating etching, and poly-Si etching. The plasma equipment simulations of the low-pressure inductively coupled plasmas are based on the Hybrid Plasma Equipment Model (developed at the University of Illinois) and include validated plasma chemical mechanisms for the relevant gas mixtures. The 2D string based feature evolution model (BabyBean) has been developed at Motorola, and it considers reactive ion etching, ion assisted physical sputtering, polymer deposition and sputtering, and isotropic etching by neutral radicals. The feature evolution model has been validated by comparing with process experiments. Simulations show that ions are able to remove "rough" protrusions on the photoresist surface through physical sputtering. This is accompanied by changes in etching or polymer deposition within "rough" cavities due to reduction in local neutral flux. Roughness evolution is sensitive to roughness amplitude and frequency.

11:40am **PS-FrM11 Ar^+/XeF_2 Beam Etching of Si: What about Doping?**, ***A.A.E. Stevens***, *E. Te Sligte, H.C.W. Beijerinck*, Eindhoven University of Technology, The Netherlands

To circumvent the complexity of plasma etching, well-defined beams of Ar^+ ions and XeF_2 etch precursor gas are used to study the fundamentals of the etch process of silicon. Ellipsometry has been applied in the beam etching experiment in an attempt to bridge the gap between beam etching and plasma etching. The ellipsometric properties of Si(100) (n-type (P), resistivity = ~ 10 Ω cm) during physical sputtering by Ar^+ ions, spontaneous etching by XeF_2 and ion-assisted etching have revealed basic information regarding the reaction layer dynamics and composition. Sputtering by Ar^+ ions results in an ion damage layer that consists of amorphous silicon (a-Si) with a surface roughness of less than 0.3 nm. The thickness of the a-Si layer can be described well with TRIM simulations. Spontaneous etching by XeF2 is found to cause a rough reaction layer up to 13 nm thick that can be thought of as a rough and (partially) fluorinated silicon (SiF_x) surface. Ion-assisted etching is a combination of sputtering by Ar^+ions and etching by XeF_2, which resembles the actual etch process in plasmas. The reaction layer in this case is a mixture of rough a-Si and SiF_x layer on top of an a-Si layer. In order to obtain a reliable comparison between ellipsometry measurements and simulations the surface roughness has to be known. Atomic force microscopy has been applied to study the surface roughness evolution of Si for various etching conditions, which has been used as input in the ellipsometry simulations. This more detailed description of the reaction layer dynamics and composition has enabled the study of n- and p-doped Si(100) samples with various types of dopants (As, Sb, P, B) and doping concentration (resistivity = 0.001-10 Ω cm). New information regarding the still unanswered question of the effect of doping on the etch mechanism will be presented.

Authors Index

Bold page numbers indicate the presenter

— T —

— U —

— V —

— W —

— X —

— Y —

— Z —