Plasma Science and Technology
Room 315 - Session PS-MoM

Critical Dimension Etching

Moderator: K. Seaward, Agilent Laboratories

8:20am **PS-MoM1 Not Quite 50 Years of Plasma Etching***, R.A. Gottscho*[1]*,* Lam Research Corp. **INVITED**

Since the advent of plasma etching in the manufacturing of semiconductor devices in the 1970s, both industry and technology have changed dramatically. In the '70s, integrated device manufacturers (IDMs) dominated the industry. IDMs built systems by starting with "sand" and using equipment of their own design and fabrication. For example, hexode etchers were created by Bell Labs, the Reinberg reactor came from Texas Instruments, and electrostatic chucks came from IBM. Today, IDMs buy plasma processing equipment with processes developed, at least partly, by the equipment companies. Fabless companies have sprouted and grown ubiquitous as foundries have become a dominant source of chip supply. In the early '80s, debates raged over the relative merits of single wafer processing for 4-6" wafers. Today, batch etchers cannot be found in the fab despite their inherent throughput advantages. Single wafer processing of 12" wafers with unprecedented control is the norm. Now, we see the advent of integrated metrology and even more advanced process control. Over this time period, gate lengths have shrunk from >1 um to

9:00am **PS-MoM3 Chemical Topography Analyses of Photoresist Patterns Exposed to HBr/O2 and Cl2/O2 Trimming Plasma Processes***, **E. Pargon**, O. Joubert, L. Vallier,* CNRS/LTM, France*; S. Xu,* Applied Materials

Nowadays, a way to bypass the lithography limitation in typical gate etch processes is to introduce a step of "resist trimming" prior all the other classical etch steps. Resist trimming induces a lateral erosion of the photoresist mask to reach a range of dimension smaller than the resolution of the lithography. To better understand the mechanisms involved in this process, an experimental procedure based on XPS has been developed to determine the chemical composition and thickness of the reactive layers formed both on top and sidewalls of the resist features during the process. The processes are performed in a high density plasma source (ICP) and two trim chemistries are investigated: HBr/O@sub2@ and Cl@sub2@/O@sub2@. The XPS analyses show that the transformations occurring on the resist sidewalls can well explain the faster trim rate obtained with a HBr/O@sub2@ chemistry. Indeed, the XPS results reveal that HBr/O@sub2@ is a very reactive chemistry leading to the formation of very thin (0.5 @nm@) reactive layers on the resist sidewalls, while when using Cl@sub2@/O@sub2@, there is a competition for the adsorption sites between atomic Chlorine and Oxygen leading in this case to thick (1.5 @nm@) carbon rich chlorine reactive layers on the resist sidewalls. Other plasma parameters (pressure, bias and source powers) have also been studied and we have obtained good correlations between the trim rate and the modifications measured by XPS on the resist sidewalls. In most cases, with the Cl@sub2@/O@sub2@ chemistry, a decrease in trim rate is well correlated with an increase in reactive layer thickness on the resist sidewalls and with a decrease of the O/Cl ratio in the reactive layer. Finally, this XPS experimental procedure enables us to better understand the mechanisms involved in resist triming processes and to determine the key plasma parameters that drive such processes.

9:20am **PS-MoM4 Aspect Ratio Dependent Etching in the Si-Treatment Process of the Source and Drain Area of sub 90 nm Devices***, **K.H. Bai**, M.C. Kim, B.Y. Nam, K.K. Chi, C.J. Kang, W.S. Han, J.T. Moon,* Samsung Electronics Co., Korea

As feature dimension shrinks down to nano scale of sub 90 nm, the aspect ratio increases up to more than 10 even at the source/drain area of the self-aligned contact (SAC) sturcture of the DRAM devices. The small open areas of the contact holes for the sub 90 nm devices require enough Si-treatment at the source/drain area to get a reliable contact resistance. However, usually the low-biased etching condition of the soft etch plasma has severe aspect ratio dependent etching (ARDE) phenomena, leading a lot of Si3N4 loss at the shoulder of SAC sturcture. To overcome the severe ARDE in the high aspect ratio structure, we investigated the ratio of radical to ion flux at the top and bottom surface of the contact holes. Because the low bias of the soft etching condition, the radicals collide to the side wall surface multiple times before reaching the hole bottom. Therefore, the radical flux at the bottom of the hole is affected by the sticking coefficient controlled by the surface temperature. However, another important key factor controlling the ARDE is the radical density in the plasma. We found that the surface coverage of the contact hole is greater than 1, the temperature becomes a less important factor in controlling the ARDE. In this work, we investigated the ARDE of our Si-treating plasma in our sub 90 nm scale devices as functions of the radical density and temperature, finding a condition nearly free from ARDE. As a result, the loss of Si3N4 at the shoulder of the gate electrode was reduced by 70%, also improving contact resistances at the source/drain more than 10%.

9:40am **PS-MoM5 Loading Effect Study on Cl@sub 2@+HBr Plasma Etching of Polysilicon***, **W. Jin**, H.H. Sawin,* Massachusetts Institute of Technology

The effect of etching product buildup, i.e. loading effect, in an inductively coupled plasma etcher for polysilicon etching with Cl@sub 2@+HBr chemistry is studied. In addition to the depletion of reactants, etching products can be fragmented upon collision with energetic electrons into various Si-containing species, with subsequent deposition on the substrate and chamber walls. The role of Si-containing species on the plasma-surface interaction has to be included in the surface kinetic model database for the simulation of etching process. This work uses real plasma beam/QCM to measure the etching yield under different ion bombardment energy and temperatures, and adds SiCl@sub 4@ in Cl@sub 2@/HBr feed gas to mimic the effect of Si-loading observed in a real ICP etcher. The study indicates that the Si-loading can reduce the etching yield significantly, due to the ion-enhanced deposition of Si-containing species on the substrate. The effect of etching yield reduction is more pronounced at lower Si-loading. The plasma beam composition was measured with a mass spectrometer as a function of feed gas composition and Si-loading. The reduction of etching yield at different Si-loading can be explained by the relative concentration of Si, SiCl and SiCl@sub 2@ species at different Si-loading. The surface composition was measured with X-ray photoelectron spectroscopy after etching. The surface composition does not show significant change with Si-loading. A surface kinetics model was developed to relate the etching yield to the beam composition, ion energy and substrate temperature. The insensitivity of surface composition to the Si-loading can also be explained by this model.

10:00am **PS-MoM6 Pattern Deformations during Resist Trimming Process and its Suppression by He-diluted O@sub 2@/SO@sub 2@ Chemistry***, **H. Morioka**, M. Tajima, M. Terahara, M. Nakaishi, I. Hanyu,* Fujitsu Limited, Japan

In addition to CD control, accuracy of pattern transcription in resist trimming and gate etching process, what is called pattern fidelity, has become more important with scaling of ULSI devices. Various pattern deformations during resist trimming, such as line-end shortening, often become serious obstacles to high-density device integration because they narrow the alignment margin and prevent the scaling of design rule. We measured line width reduction (amount of trimming) and the line-end shortening during trimming and gate etching process. Experiments were performed on an ICP etcher. O@sub 2@-base chemistry was used to "trim" resist patterns. The gate stack consisted of 1nm gate oxide, 100nm Poly-Si, and 30nm SiO@sub 2@, which was coated by organic BARC and patterned by ArF lithography. We found that the line-end shortening was larger than the line width reduction, and this disparity increased with increasing trimming time, which was accompanied by pattern deformations in specific patterns, such as L-shape corner. This pattern dependent resist erosion can be related to excessive etchant flux in the convex area. In order to suppress these disparity and pattern deformation, we investigated He/O@sub 2@/SO@sub 2@ chemistry, in which SO@sub 2@ was a source of lateral etching inhibitor that is mild to ArF resist, and oxygen was main etchant of trimming. He-dilution was used to control the trimming rate and suppress condensation of sulfur compounds. Optimizing etchant/inhibitor ratio by means of O@sub 2@/SO@sub 2@ ratio, we have succeeded in reducing line-end shortening and suppressing pattern deformations for trimming of sub-100nm resist patterns. In optimized conditions, trimming amount was almost the same as line-end shortening, and proximity effect (dense-iso differnce) of trimming was smaller than 5nm. Therefore we have fabricated 25nm gate poly-Si patterns by He/O@sub 2@/SO@sub 2@ trimming (from 80nm to 25nm) and conventional poly-Si gate etching process.

10:20am **PS-MoM7 On the Roughness of Etched Silicon***, **A.A.E. Stevens**, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

The smaller the etched features, the more important the roughness of the etched feature surface becomes. Not only for integrated circuits, but also

[1] **AVS 50th Anniversary Invited Speaker**

for, e.g., photonic crystals, the surface roughness might limit the device quality. By using in situ (spectroscopic) ellipsometry and mass spectrometry, the effect of Ar@super +@ ions and XeF@sub 2@ etch precursor on the etch mechanism has been studied, simultaneously collecting information regarding the roughness evolution. Analysis of the XeF@sub 2@ reactivity and SiF@sub x@ products in contrast to the reaction layer composition shows that the reaction layer thickness, i.e. the surface fluorine content, scales with the roughness. This implies, that the SiF@sub x@ layer build up suggested in literature can be explained by the increasing roughness of the surface, thus the effective surface area increase of the etched Si samples. Furthermore, the etched Si samples have been analyzed with an AFM for comparison with the in situ ellipsometry results. The same trends in roughness evolution have been observed for the ellipsometry measurements and the AFM measurements, corroborating the used ellipsometry models. To learn about the role of the etch precursor and ions in the roughening of the surface during etching, the Family-Vicsek scaling theory of the surface roughness has been applied. The scaling coëfficients @alpha@ and @beta@, representing lateral correlations on the surface and time dependent roughness evolution, respectively, have been derived from the AFM data analysis. Since specific @alpha@ and @beta@ values are related to the surface processes occurring during the etching, the application of the scaling theory aids in understanding the role of the ions and etch precursor in the roughening process.

10:40am **PS-MoM8 Investigation of Trim Etching Process for Formation of Si/High-K Gate Stack***, K.M. Tan,* National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; L. Chan,* Chartered Semiconductor Manufacturing, Singapore

In recent years, a photoresist trimming technique based on the current 248nm and 193nm lithography technology are being developed to achieve smaller gates. In this work, we investigated the trimming technique to directly apply to the etching of the Si/SiO@sub 2@ and Si/HfO@sub 2@ gate stacks to further reduce the gate length. The trimming process developed using an industry standard ICP etcher consists of a main etch step followed by a trimming step using HBr, SF@sub 6@ and Cl@sub 2@. When HBr and SF@sub 6@ were used, a Si layer was trimmed at the rate of 17nm per minute at a pressure of 80mTorr, a bias power of 60W and an inductive power of 400W. A higher trim rate was obtained by using a higher inductive power and also by replacing HBr with Cl@sub 2@. However, the use of Cl@sub 2@ resulted in the decrease of the selectivity of Si to the underlying SiO@sub 2@, and thus reduced the maximum allowable trimming time. The trimming rate varied with pressure with an initial increase from 40mTorr to 70mTorr and a subsequent decrease from 70mTorr to 80mTorr. According to the results obtained for all the etch conditions used, HfO@sub 2@ produced a much slower etch rate than SiO@sub 2@ regardless of whether Cl@sub 2@ or HBr was used, and this resulted in a higher etch selectivity of Si to the underlying dielectric. As a result, a longer trimming time was allowed for HfO@sub 2@ than SiO@sub 2@. It was interesting to find out that an etching profile after the trimming step could be more anisotropic than that before the trimming step. Further studies are in progress to obtain 65nm trimmed gate structures from 130nm patterns using the 193nm photolithography technology.

11:00am **PS-MoM9 50nm Gate Electrode Patterning using a Neutral Beam Etching System***, **S. Noda**, S. Samukawa,* Tohoku University, Japan*; H. Nishimori, T. Ida, T. Arikado,* Semiconductor Leading Edge Technologies, Inc. (Selete), Japan*; K. Ichiki,* Ebara Research Co., Ltd., Japan

The increased packing density of ultra large-scale-integrated circuits (ULSI) requires ultra thin dielectric films that have low leakage current and are extremely reliable in metal-oxide-silicon (MOS) devices. High-k dielectrics films have been identified as leading candidates to replace conventional SiO@sub 2@ gate dielectrics in future ultra large-scale integrated circuits. However, the high-k films are more fragile and defective materials in comparison with the SiO@sub 2@-based thin films. As a result, the process-induced damages are very serious problems, such as charge-build-damages, changes in film quality and generation of defects by the irradiation of charged particles (ions and electrons) and VUV photons during the plasma etching processes. To break-through these problems, we developed a high-efficiency neutral beam etching system using negative ions generated in the pulse-time-modulated inductively coupled plasma (TM-ICP).@footnote 1@ In this system, high-density (1-4mA/cm@super 2@) and low-energy (10-100eV) neutral beams are effectively extracted from the pulsed plasma. It is expected that the neutral beam etching is promising candidate for the damage-free high-k gate electrode patterning. In this paper, we evaluated characteristics of the poly-Si gate etching using fluorine (SF@sub 6@) and chlorine (Cl@sub 2@) based gas chemistries. Highly anisotropic 50nm poly-Si etching profiles could be obtained with no degradation of extremely fine resist patterns in the case of the chlorine based neutral beams. The electrical properties of MOS capacitors will also be presented in comparison with the results in the conventional plasma etching systems. @FootnoteText@ @footnote 1@ S. Samukawa, K. Sakamoto and K. Ichiki, J. Vac. Sci. Technol. A20, 1566 (2002).

11:20am **PS-MoM10 Surface and Reactor Dynamics Governing Photoresist Trim and Organic BARC Open Plasma Processing***, **D.J. Cooperberg**,* Lam Research Corporation*; S. Johnston, D. Horak,* IBM Microelectronics*; V. Vahedi,* Lam Research Corporation

Photoresist trimming is employed to obtain acceptable feature profiles in sub-130nm linewidths. For logic applications, the process offers a means of shrinking gate length to values that are smaller than can be printed directly with a chosen lithographic technology. When organic bottom anti-reflective coatings (O-BARC) are used to assist photolithography the photoresist trimming can be performed before, during, or after an in-situ O-BARC opening process. The trimmed PR and opened O-BARC are used as a mask for either a hardmask open or a gate etch process. In this talk we will present process trends for O@sub 2@/CF@sub 4@/N@sub 2@ photoresist trim and O-BARC open plasma processing. We have measured the effect of several reactor settings as well as wafer topology on vertical and trim (lateral) etch rates. Reactor settings studied include inductively coupled power, bias power, gas mixture, and electrode temperature. In addition, the effects of variations in exposed area, local pattern density, and microloading or aspect ratio have been studied. It will be shown that local pattern density gradients over a length scale @>=@ the gas mean free path can effect etch uniformity. Trim rates are measured during the O-BARC open process and the trim process separately. It will be shown that the dependence of trim rate on aspect ratio changes dramatically during these two steps. Our experiments are used to identify the appropriate semi-empirical models for the surface kinetics and intra-feature transport which govern feature scale profile evolution. Additionally our experiments can be used to partially characterize reactor dynamics and the transport of the primary etchant, O atoms.

11:40am **PS-MoM11 3-Dimensional Modeling of Pulsed Inductively Coupled Plasmas: A Method to Improve Uniformity@footnote 1@***, **P. Subramonium**, M.J. Kushner,* University of Illinois at Urbana-Champaign

Continuous wave (CW) operation of inductively coupled plasma (ICP) reactors having asymmetric pump ports or feedstock gas injection may produce asymmetric densities of radicals and fluxes to the substrate. These asymmetries are often intensified by positive feedback between regions of higher conductivity producing higher power deposition and higher ionization rates, which in turn increase the conductivity. Pulsed ICPs have been investigated as a means to extract negative ions to the substrate to reduce charging damage. Pulsed ICPs may also provide a means to reduce or eliminate asymmetries by reducing this positive feedback. In this paper, results from a 3-dimensional model for pulsed ICPs having such asymmetries will be discussed. As these long-term phenomena are difficult to resolve in multi-dimensional plasma equipment models a computationally parallel hybrid model has been developed to both speed the calculation and to better represent the physical processes. Results for pulsed ICPs in Ar, Ar/Cl@sub 2@, Ar/C@sub 2@F@sub 6@ gas mixtures will be discussed while varying pulse repetition frequency (5 - 20 kHz), duty cycle (10% - 70%), power (200 - 800 W) and pressure (5 - 20 mTorr). We found that the non-uniformities in species densities which feedback through the plasma conductivity are generally reduced during the afterglow of the pulsed plasma. In the afterglow, without the nonuniform source function, diffusion smooths the plasma density profile, providing a more uniform set of initial conditions for the next power pulse. The ionization source during the subsequent power pulses is therefore more uniform. As a result, time averaged plasma properties for pulsed plasmas are more uniform compared to CW excitation. Uniformity generally improves with decreasing duty cycle and decreasing repetition rate. @FootnoteText@ @footnote 1@ Work supported by Semiconductor Research Corporation and National Science Foundation.

Plasma Science and Technology
Room 315 - Session PS+MM-MoA

MEMS Etching
Moderator: F.G. Celii

2:00pm **PS+MM-MoA1 Understanding Deep Silicon Etching: Mechanisms for Formation and Removal of Sidewall Passivation*, M.L. Steen,*** IBM T.J. Watson Research Center*; T.J. Dalton,* IBM Semiconductor Research and Development Center*; C.K. Tsang, R.W. Nunes, J. Vichiconti, E.A. Sullivan, B.N. To, D. Barrett,* IBM T.J. Watson Research Center

One of the interesting aspects of deep silicon etching is the diversity of process requirements. In addition to high throughput, many applications have added demands on profile shape and surface morphology. Supporting such applications hinges on rational control of sidewall passivation. Two fluorine-based methods are used to achieve high silicon etch rates, each with its own variation of sidewall passivation. Most widely used is time-multiplexed deep etching (TMDE), wherein the etching and passivating cycles are performed sequentially. Sidewall passivation is accomplished via polymer deposition at room temperature. Alternately, a second method involves cryogenic cooling of the wafer to reduce lateral etching. However, problematic to both of these processes, the thickness of the sidewall-passivating layer is not uniform with etch depth. In cryogenic etching, the blocking layer is very thin, thereby making it difficult to maintain a consistent thickness over the entire etch depth. In TMDE, the thickness of the polymer covering decreases rapidly at greater depths and lateral etching increases there to form an undesirable bowed or barreled etch profile. This is particularly problematic for applications that have tight specifications for sidewall structure. Our goal is to understand the role the passivating layer plays in the formation of sidewall structure. Toward this goal, a number of process variables were explored using a commercial, inductively-coupled plasma etcher. We report a method that tailors the shape of the profile through better control of the formation and subsequent removal of the passivating layer. A significant increase in the silicon etching rate, minimization of mask undercut, and substantial reduction in bowing will be discussed. Overall, our method demonstrates enhanced process performance and flexibility to meet a broad range of needs in deep silicon etching.

2:20pm **PS+MM-MoA2 Improvement of Anisotropy and Aspect Ratio of a Pattern Etched in Bosch Process by using a Faraday Cage*, J.-H. Min,*** *G.-R. Lee, J.-K. Lee, S.H. Moon,* Seoul National University, Korea*; C.-K. Kim,* Ajou University, Korea

Bosch process, which consists of sequentially alternating etch and deposition steps using SF@sub 6@ and C@sub 4@F@sub 8@ plasmas, has been widely used for deep silicon etching in the fabrication of MEMS due to its advantages for obtaining patterns of high aspect ratio and anisotropy. Because the opening sizes of many MEMS structures are considerably large (about 1~100 µm), the electric field at the convex corner of a micro feature is locally distorted such that ions travel inside the etched pattern with a broad angular distribution. As a result, the flux of ions incident on the bottom surface is decreased with an increase in the etch depth, which eventually limits the maximum aspect ratio obtained in Bosch process. This limiting factor cannot be overcome by optimizing process variables. In this study, a Faraday cage, defined as a box made of conductor walls, was used to overcome this limitation. In the Faraday cage system, ions enter perpendicular to the sheath formed along the top grid plane of the cage and travel inside the cage maintaining the initial incident direction because electric potential in the cage is unaffected by outside voltages and therefore is the same throughout. Accordingly, the trajectory of ions, which has a narrow angular distribution determined by the grid pitch of and the sheath thickness on the top plane, is not changed at the convex corner of the micro feature or inside the pattern located in the cage. It was confirmed by an ion angular-energy distribution analyzer that the angular distribution of ions entering the pin hole of 10-µm-diameter, which is the same as the size of pattern opening, is narrower in the cage system than in the case of no cage. As a result, the aspect ratio and the anisotropy of the etched pattern were improved by using a Faraday cage in Bosch process.

2:40pm **PS+MM-MoA3 Exploring Microdischarges for Manufacturing and Sensing Applications*, Y. Gianchandani,*** University of Michigan **INVITED**

The increasing diversity of applications in microsystems for sensing and actuation motivates a significant amount of research in lithography-based fabrication techniques. The general goals for these processes include the facilitation of structural complexity and material diversity, amongst others. This talk will address how microplasmas (which are ignited between co-planar or stacked thin film metal electrodes patterned on a single wafer surface) can facilitate certain types of structural complexity by permitting materials such as Si to be etched in unique ways; and how micro-arcs (which are ignited between a micromachined electrode array and planar workpiece) can facilitate material diversity by permitting stainless steel and other metals to be micromachined for devices such as cardiac stents. Beyond manufacturing issues, the ability to predict and control microdischarges permits them to be exploited in transduction schemes. Spectroscopic sensing of chemicals in both gas and liquid phase is an obvious application. For example, microdischarges to liquid microchannels have been used to detect inorganic contaminants such as lead and chrome in water. However, the converse application, which is the use of liquids to serve as inexpensive but tunable sources for radiation wavelengths that are otherwise not easy to generate, may also offer value. These issues will be addressed as well.

3:20pm **PS+MM-MoA5 Feature Scale Model of Etching High Aspect Ratio Structures in Silicon using SF@sub 6@/O@sub 2@ Plasma*, J. Belen,*** *S. Gomez,* University of California, Santa Barbara*; M.W. Kiehlbauch, D.J. Cooperberg,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

The need to etch high aspect ratio features (depth-to-width) such as deep holes and trenches in Si arises in manufacturing of microelectromechanical systems and capacitors in memory devices. Anisotropic plasma etching of such features is achieved by taking advantage of energetic ion bombardment of the surface in the normal direction in conjunction with sidewall passivation with a film that is resistant to etching. Feature profile evolves as a result of various ion-assisted etching, passivation and deposition processes that occur on the feature surfaces. A fundamental and quantitative understanding of the balance between these processes is necessary for achieving control over the feature profile shape. We have developed a semi-empirical feature scale model of Si etching in an SF@sub 6@/O@sub 2@ plasma. This model is used to quantify etching kinetics and to identify the important parameters that affect profile evolution. Information from plasma diagnostics and previously published data are used to estimate F, O, and ion fluxes as well as ion energy and angular distributions. These estimates are used as input to the profile simulations in order to reduce the degrees of freedom in the model. Experimentally inaccessible parameters such as the spontaneous chemical etch rate constant, F and O sticking coefficients, ion-enhanced etch yield and ion scattering parameters are determined by matching the experimentally observed and simulated feature profiles under different plasma etching conditions. The mask undercut and the slope of the feature sidewalls are controlled by the F-to-O flux ratio. Two distinct mechanisms for sidewall passivation are identified: (a) surface oxidation, which is thought to be prevalent at high and intermediate F-to-O ratios where the sidewalls are either negatively tapered (bowed out) or vertical, and (b) redeposition of reaction products, which results in positively tapered sidewalls at low F-to-O ratios.

3:40pm **PS+MM-MoA6 Etching of High Aspect Ratio Structures in Si using SF@sub 6@/O@sub 2@ Plasmas*, S. Gomez,*** *J. Belen,* University of California, Santa Barbara*; M.W. Kiehlbauch,* Lam Research Corporation*; E.S. Aydil,* University of California, Santa Barbara

Plasma etching of high aspect ratio (depth-to-width) structures in Si is a crucial step in manufacturing trench capacitors for memory devices, and integrated components for microelectromechanical systems (MEMS). We have investigated etching of deep features (~10 µm) with high aspect ratios (~50) using plasmas maintained in mixtures of SF@sub 6@ and O@sub 2@ gases. The etching experiments were conducted in a low pressure (5-80 mTorr), high density, inductively coupled plasma etching reactor with a planar coil to maintain the discharge and with radio frequency (rf) biasing of the substrate electrode to achieve independent control of the ion flux and ion energies. Specifically, we have studied the effects of pressure, rf-bias voltage and SF@sub 6@-to-O@sub 2@ gas ratio on the etch rate, feature profile and selectivity using Si wafers patterned with 0.5-0.35 µm diameter holes in a SiO@sub 2@ mask. Visualization of the profiles using SEM is complimented by plasma diagnostics such as optical emission spectroscopy in conjunction with actinometry and mass spectrometry to understand the key factors that control the anisotropy, selectivity and etch rate. Oxygen ionization and dissociation products (O and O@super +@) oxidize the feature sidewalls and help achieve anisotropic etching through the sidewall passivation mechanism. F-to-ion flux ratio and F-to-O flux ratio are found to be the important internal plasma parameters that determine

the etch rate and anisotropy. The mask undercut and the slope of the sidewalls is determined by the F-to-O ratio in the plasma. Increasing the SF@sub 6@-to-O@sub 2@ ratio in the feed gas increases F-to-O ratio and makes mask undercutting worse because passivation by O atoms cannot keep up with chemical etching by F atoms. As F-to-O ratio is decreased, effective sidewall passivation by O atoms results in nearly vertical sidewalls. Further reduction in F-to-O ratio results in sidewalls that slope inwards towards the bottom of the feature.

4:00pm **PS+MM-MoA7 Via Drilling on Silicon Wafers using the Cryogenic Process***, **T. Tillocher**, A. Basillais, X. Mellhaoui, P. Lefaucheux,* GREMI, France*; M. Boufnichel,* ST Microelectronics*; R. Dussart, P. Ranson,* GREMI, France

Plasma etching has an important place in microelectronics and microsystems industries. Some techniques, especially Bosch and cryogenic processes, enable the realization of high aspect ratio structures. The Bosch process is widely used in spite of scalloped profiles whereas the cryogenic process is quicker and presents smooth etched surfaces. Via (12 µm in diameter) drilling on silicon wafers is achieved by cryogenic etching in an industrial ICP reactor (Alcatel 601E). A SF6/O2 plasma is created and expands toward a polarized and cooled silicon wafer. Plasma parameters are optimised so as to obtain vias with an anisotropic profile with a high etch rate. End to end vias were performed with an average etch rate about 7µm/min by etching separately the two sides of the wafer. Yet, all of them did not meet right in the middle of the plate as it should be and their shape is not reproducible in the whole wafer. This seems to be due to a non enough homogeneous cooling system. Moreover, some defects, such as bowing and undercut lead to an increase of the final diameter of the via and hence must be limited. A process including a soft etching step, an over-passivating step, and a standard etching step leads to a significant reduction of these defects. O2/SF6 ratio is adjusted in the two first steps. Additionally, it was shown that bias voltage has a strong influence on the profiles : its increase is not synonym of a deeper etching but a slightly greater volume etched. Crystal orientation dependent etching also appeared at lower temperatures and particularly in the direction what can explain negative slopes in this cases.

4:20pm **PS+MM-MoA8 Si, SiO@sub 2@ Feature Etching for MEMS Fabrication: A Combined Simulator Coupling Local Transport, Surface Etch, and Profile Evolution Models***, **G. Kokkoris**, C. Boukouras, A. Tserepi,* National Center for Scientific Research (NCSR) "Demokritos", Greece*; A.G. Boudouvis,* National Technical University of Athens (NTUA), Greece*; E. Gogolides,* National Center for Scientific Research (NCSR) "Demokritos", Greece

Profile control during feature etching is a central requirement in the manufacturing processes of microelectromechanical systems (MEMS) or microelectronics devices. Simulation of the feature profile evolution can contribute to this challenge. The purpose of this work is a complete simulator for feature etching. The goal is to predict the effect of the bulk plasma phase to the feature profile, and is accomplished through the coupling of the following component modules: 1) a local transport model: local fluxes of neutrals and ions inside features are calculated taking into account shadowing and re-emission phenomena.@footnote 1@ 2) a surface etch model: local etch rates at each elementary surface of the structure are calculated through site balances. Si, SiO@sub 2@ substrate etching models under fluorine or fluorocarbon plasmas have already been developed.@footnote 2@ 3) a profile evolution algorithm: the level set method@footnote 3@ is fed with the local etch rates and moves the feature profile. The complete simulator can be used to a) validate suggested surface models through comparison with experimental data, b) investigate and explain the influence of feature size and surface morphology on etch rates (e.g. reactive ion etching lag phenomenon@footnote 4@, effect of roughness on etch rates) and c) simulate and optimize processes such as the BOSCH process@footnote 5@ for the etching of high aspect ratio Si structures, where pulsed alternating flows of SF@sub 6@ and C@sub 4@F@sub 8@ gases are used. @FootnoteText@ @footnote 1@V. K. Singh, E. S. G. Shaqfeh, and J. P. McVittie, J. Vac. Sci. Technol. B 10, 1091 (1992).@footnote 2@E. Gogolides, P. Vauvert, G. Kokkoris, G. Turban, A. G. Boudouvis, J. Appl. Phys. 88, 5570 (2000).@footnote 3@J. A. Sethian, J. Comp. Phys. 169, 503 (2001).@footnote 4@G. Kokkoris, E. Gogolides, A. G. Boudouvis, J. Appl. Phys. 91, 2697 (2002).@footnote 5@F. Larmer, A. Schilp, German Patent DE 4241045.

4:40pm **PS+MM-MoA9 In-Situ On-wafer Monitoring for Charge Build-up Voltage during Plasma Process***, **T. Shimmura**, S. Soda, M. Koyanagi, K. Hane, S. Samukawa,* Tohoku University, Japan

High-aspect-ratio SiO@sub 2@ contact hole etching is one of the key processes in the fabrication of ULSI devices. However, charge accumulation in contact holes during etching is one of the main causes of serious problems, such as charge-build-up damage, etching-stop, and microloading effects. Therefore, it is very important for realization of the next generation semiconductor devices to understand the mechanism of such electric charge accumulation and to be in control of plasma processes. As a result of our previous research, it was clear that deposited fluorocarbon film in contact holes shows high electric conductivity by ion irradiation.@footnote 1@ This paper reports on in-situ on-wafer monitoring for the build up charging potential during plasma processes. We were developed the device used for measuring charging potential. This device consists of Poly-Si(300 nm)/SiO2(1.7 µmm)/Poly-Si(300 nm) stacked layer structure. The contact hole of 300 nm diameter is formed to top Poly-Si layer and SiO@sub 2@ layer, and the numbers of holes were 6,400,000. The potential of top and bottom Poly-Si electrode were measured during plasma exposure with/without deposited fluorocarbon film. The potential difference between top and bottom Poly-Si electrode without the deposited fluorocarbon film is about 70 volts. On the other hand, in the case that the deposited fluorocarbon film exists on sidewall, the potential difference between top and bottom electrode was hardly observed. This result shows that the sidewall deposited fluorocarbon film has high electric conductivity and mitigates the electric charge accumulation at the contact hole bottom during SiO@sub 2@ etching processes. @FootnoteText@ @footnote 1@ T. Shimmura, S. Soda, S. Samukawa, M. Koyanagi and K. Hane, J. Vac. Sci. Technol. B, 20 2346 (2002).

5:00pm **PS+MM-MoA10 Plasma Etching of Chromium as a Hard Mask for a Complex Metal Stack Etch***, **D. Cruz**,* UCLA/Sandia National Laboratories*; M.G. Blain,* Sandia National Laboratories*; J.P. Chang,* University of California, Los Angeles

We have investigated the etching of chromium in an inductively coupled plasma (ICP) reactor and its etching selectivity to Al and SiO@sub 2@. Chromium is being utilized as a hard mask in etching a three-layer aluminum/silicon dioxide metal stack to form a self-aligned structure of 4µm in depth. The stack comprises the basis for a micro-cylindrical ion trap mass analyzer. The chromium etching chemistry was chlorine based, with the addition of He, Ar, and O@sub 2@. The Cr samples, approximately 2500 Å thick, were e-beam evaporated on two and three layers of Al/SiO@sub 2@ stacks. Chemical vapor deposited silicon dioxide was used as a hard mask to pattern Cr into 2-micron sized features. The selectivity of chromium to silicon dioxide during the He/Cl@sub 2@/Ar/O@sub 2@ chromium etch was 15:1. During the main chromium etch, the etch rate was determined to be approximately 1500 Å/min, at a pressure of 10 mTorr and 250 V DC bias. The He/Cl@sub 2@/Ar/O@sub 2@ discharge provided a fast etch rate with no plasma induced damage. Once the chromium was patterned, the Al/SiO@sub 2@ stack was exposed to an ICP Al etch, utilizing a Cl@sub 2@/BCl@sub 3@ based plasma chemistry, followed by an ICP SiO@sub 2@ etch, utilizing SF@sub 6@/Ar/N@sub 2@/O@sub 2@. These two chemistries were used alternatively until all layers of the stack were etched through in a self-aligned fashion. The etch rate ratios of Al and SiO@sub 2@ to chromium were 70:1 and 25:1, respectively. The overall final stack etch totaled about 22 minutes. No grassing or sputtering was noted on the sample, however profile control of the Al layer is an issue due to the lack of a sidewall forming polymer source. Chromium seems to be a promising hard mask, having high selectivity to the ICP Al etch and ICP SiO@sub 2@ etch. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Plasma Science and Technology
Room 314 - Session PS-MoA

Plasma Sources

Moderator: E.V. Barnat, Sandia National Laboratories

2:00pm **PS-MoA1 Ion-Acoustic Solitons in a High Power Pulsed Magnetron Sputtering Discharge***, K.B. Gylfason,* University of Iceland, Iceland*; **J. Alami**, U. Helmersson,* Linkoping University, Sweden*; J.T. Gudmundsson,* University of Iceland, Iceland

We report on the formation of ion acoustic solitons in an unipolar pulsed magnetron plasma. A high density plasma > 10@super 18@ cm@super -3@ is created by applying a high power pulse (6-17 J) with pulse length 100 µms and repetition frequency 50 Hz to a planar magnetron discharge. The temporal behaviour of the electron density measured by a Langmuir probe shows oscillations as the plasma density decays. We relate these oscillations to solitons traveling away from the target followed by stationary oscillations. The velocity, width, and amplitude characteristics of the soliton are discussed and compared to the properties of the soliton solutions of the Korteweg-de Vries equation. The speed of the soliton along the axis of the discharge decreases with increased gas pressure. We relate this decrease in travelling speed to the decrease in the fractional density modulation dn/n@sub 0@.

2:20pm **PS-MoA2 Next Generation RF Ion Beam Source for Three-Dimensional and other Critical Etching Applications***, **A.V. Hayes**, V. Kanarov, R. Yevtukhov, C. Borges, K. Williams, M. Campo, B. Druz,* Veeco Instruments, Inc.

Rf plasma broad ion beam etch technology is used in manufacturing of magnetic, optical, and other types of thin film devices due to its unique capabilities to etch difficult materials and control ion energy and incidence angles. Requirements for increased critical dimension (CD) control and directional "static etch" processes have started to exceed the ion current density and directionality uniformity capabilities of conventional ion sources. "Static etch" processes in which the substrate is tilted at ion incidence angles of up to 70°-80° with no or only partial substrate rotation, are particularly challenging, requiring the ion beam to be very uniform and collimated across a three dimensional space within the beam occupied by the wafer. Development of a novel rf ICP broad ion beam source with dynamic plasma magnetic field configuration designed to achieve these requirements will be described. In addition, the role of the beam divergence angle and other beam dispersion parameters on the CD and static etch uniformity will be discussed. Results will be measured in terms of etch uniformity on silicon oxide coated wafers and etch divergence using a shadow mask type measurement fixture. In an optimum configuration the source is capable of achieving a uniformity of less than 1% sigma/mean on a static wafer (about a 4-5X improvement compared with current technology sources) and less than 0.5% on a rotated wafer (a 2-3X improvement) with excellent repeatability. The full etch divergence angle is less than 3°, and uniform across the substrate within 0.5°. Other applications of this source could include uniform etching of features mounted on 3-dimensional substrates.

2:40pm **PS-MoA3 The Use of Reactive Gases with Broad-beam RF Ion Sources for Industrial Applications***, **St. Schneider**,* Forschungszentrum Juelich, Germany*; T.W. Jolly,* Oxford Instruments Plasma Technology Ltd.*; H. Kohlstedt, R. Waser,* Forschungszentrum Juelich, Germany

Broad-beam ion sources are used for a number of important industrial etching and deposition applications, and the use of inductively-coupled plasmas has greatly increased the feasibility of using beams of reactive gases, especially of chlorine and oxygen, but also of CO, CO@sub 2@, CF@sub 4@, CHF@sub 3@, SF@sub 6@ etc. In order to gain more understanding of the factors that affect the composition of beams of these gases, we have used a Hiden energy-dispersive quadrupole mass spectrometer to analyze the flux of ions and energetic particles produced by an Oxford Instruments 15cm RF ion source. For all of the above gases, we have analyzed the effects of changing the operating conditions on the composition of the ion beam, and the fractional production of multiply-charged ions; on the plasma potential (and the consequential divergence of the ion beam) and on the spread in energy of the ion beam. We discuss how these factors influence the correct use of the ion source in etching applications with these gases. It is important that the design of the ion source should be optimized for the process gases that are used. The source was originally optimized for use on argon. We discuss the effect of the design on the source's performance with the different gases, and we consider whether design changes could be appropriate for optimum performance on different gases.

3:00pm **PS-MoA4 Reactive Sputter Deposition of Nanocrystalline Compound Thin Films with a Hollow Cathode Source Operated in a Static Mode***, **A. Pradhan**[1], S.I. Shah,* University of Delaware

Hollow Cathode Sources (HCS) are unique sputtering sources that sputter material from the inner surface of a cylindrical tube. Due to their geometry, HCS offer several advantages such as lack of hysteresis, low consumption of the reactive species, high plasma density and high deposition rates. We have characterized a titanium HCS for reactive deposition of titania films in static mode. In this mode the sputtering is carried out in a static gas volume. Stoichiometric films growth could be sustained even after 3 hours of continuous sputtering. This new method of reactive sputtering offers several advantages over conventional techniques such as ease of operation, lower equipment cost, lower environmental load, etc. Langmuir probe measurements were used to determine the plasma parameters in a static HCS. The plasma density was 2-3 orders of magnitude greater than that obtained in planar sputtering. The high-density plasma can be used to deposit stoichiometric nanocrystalline oxide films by negatively biasing the substrate and allowing the ion bombardment to provide the energy required for crystallization of the growing film. X Ray Diffraction (XRD) of the films grown with a substrate bias of -80V shows the presence of the rutile phase. The particle size was estimated from the XRD peak broadening to be around 20nm. The films were also characterized by X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Films were found to be nanocrystalline only when the sputtering gas was rich in oxygen. Monte Carlo simulations were carried out using SRIM program to determine the energy transferred by the ions to the growing surface. It was found that backscattered ion count was much higher in the case of O2 when compared to Ar, which could be responsible for the formation of nanocrystalline films.

3:20pm **PS-MoA5 Evolution of Radiofrequency Plasma Sources***, **F.F. Chen**[2],* University of California, Los Angeles **INVITED**

Though this is the 50th AVS Symposium, RF plasma sources have a shorter history. Their development, driven by the explosive growth of the computer industry, did not really start until the 1970s. There are three main types: capacitive discharges called Reactive Ion Etchers (RIEs), Inductively Coupled Plasmas (ICPs), and the newcomer on the block, Helicon Wave Sources (HWS). Development of RIEs and ICPs has progressed mainly by trial and error, but in the last ten years their evolution has been aided by computer modeling, a result of the fast chips that these sources themselves make possible. From a plasma physics standpoint, each of these sources poses interesting problems. RF energy penetrates into ICPs much farther than skin depth theory would predict. Helicon sources produce much higher densities than ICPs at the same power. RIEs, with all their deficiencies, still perform better in many applications. Are we simply lucky, or are there physical reasons for this?

4:00pm **PS-MoA7 Physics of High-pressure Helium and Argon Plasmas***, **M. Moravej**, S.E. Babayan, X. Yang, G.R. Nowling, R.F. Hicks,* University of California, Los Angeles

The physics of helium and argon plasmas was investigated in the pressure range of 10 to 1000 Torr. The current and voltage waveforms and the current-voltage plots were obtained at varying pressures for both gases. The waveforms indicated that before the plasma was struck the load was purely capacitive for both gases, however, after the discharge was ignited, the argon plasma exhibited a greater resistive nature than the helium. The IV curves at 760 Torr indicate that the breakdown voltage for argon was approximately 500 V higher than that of helium. From these IV measurements, the helium and argon plasma densities were calculated to be 3.48*10@super 11@ and 3.15*10@super 11@ cm@super -3@, respectively and the electron temperatures were determined to be 1.3 and 0.3 eV, respectively. The effect of pressure and of impurities, O@sub 2@ and CF@sub 4@, on the physics of the plasma was investigated by these measurements and will be presented at the meeting.

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

[2] **AVS 50th Anniversary Invited Speaker**

4:20pm **PS-MoA8 Two-dimensional Self-consistent Modeling of Wave Propagation and Plasma Dynamics in a Helicon Source*, D. Bose,*** Eloret Corp.*; T.R. Govindan, M. Meyyappan,* NASA Ames Research Center

Helicon plasma sources are of interest in a variety of applications such as space plasma propulsion, fusion experiments, materials processing reactors, etc. The interest in these devices stems from their ability to generate high density plasmas by efficiently absorbing the applied radio frequency power. In this paper we will present results form a two-dimensional helicon plasma model that enforces self-consistency between wave propagation and plasma dynamics. Plasma fluid equations relevant for plasma generation, heating, and transport with externally applied dc magnetic field are solved self-consistently with Maxwell's equations for rf electric field, Ohm's law for rf plasma current, and space charge waves. The absorption and propagation of Trivelpiece-Gould waves generated due to a finite electron mass are implicitly included. This wave is highly dissipative and is the chief mode of energy transfer to the plasma. A parametric study will be performed to isolate the factors that affect bulk versus peripheral power absorption, downstream plasma density and uniformity. The effect of altering the dc magnetic field on plasma and wave characteristics will be presented. Our current results show that the applied magnetic field profile can be adjusted to move the peak plasma density from the near antenna source region to the process chamber. Comparisons with the available experimental data on plasma density and uniformity will also be presented.

4:40pm **PS-MoA9 Large Area Electron-Beam Generated Plasma Processing System@footnote 1@***, **D. Leonhardt**, C. Muratore, S.G. Walton,* Naval Research Laboratory*; D.D. Blackwell,* SFA Inc.*; R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

NRL has developed a 'Large Area Plasma Processing System' (LAPPS) using an electron beam (e-beam) to initiate the gas ionization process with the goal being the increased control over the flux of reactive species to the surface and the ability to modify surfaces over large areas. Our system demonstrates that the e-beam ionization process is largely independent of gas composition and capable of producing low temperature plasma electrons in high densities over large areas (square meters). The system consists of a planar plasma distribution generated by a magnetically collimated sheet of 2 keV, < 1 mA/cm@super 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 (100-200 Gauss) for plasma localization. This presentation will focus on (1) the production of a large area (> 0.5 m@super 2@) system and (2) applications of these plasma sources for surface modification. Construction, scaling and uniformity at the substrate in the large plasma source will be discussed, including the processing stage configurations and layout. General characteristics of these plasmas will be discussed and illustrated through time-resolved in situ plasma diagnostics (Langmuir probes, microwave transmission and mass spectrometry). @FootnoteText@@footnote 1@ Work supported by the Office of Naval Research@footnote 2@ Muratore, C., NRL/ASEE Postdoctoral Research Associate.

5:00pm **PS-MoA10 Post-etch Wafer Cleaning by a New Dry-cleaning Technique using Both Gas Flow and Plasma*, Y. Momonoi,*** *K. Yokogawa, M. Izawa,* Hitachi Ltd., Japan

Because wafer cleaning ultimately affects yield and reliability, it is one of the crucial issues in fabricating semiconductor devices. Regarding devices, scaling-down and adoption of new materials impose an imminent demand for new developments in particle cleaning. Dry-cleaning techniques have been proposed recently as other approaches for particle removal. Their removal efficiency, however, is less than that of wet cleaning, because it is difficult to balance chemical cleaning and physical cleaning. In light of the above circumstances, the authors have developed a new concept of dry particle cleaning, named dry scrubber.@footnote2@ The dry scrubber utilizes both the mechanical effects of gas flow and the chemical effects of a down-flow plasma. Regarding the gas flow, narrowing the flow space along the wafer increases the viscous friction, which causes particles to remove from the wafer surface, and they are transported away. Regarding the plasma, a gas mixture of CF@sub 4@ and O@sub 2@ is induced in it, which weakens the adhesion force of particles chemically. The basic cleaning capabilities of the dry scrubber were evaluated by using it to remove Al@sub 2@O@sub 3@ particles on 8-inch p-type bare silicon wafers. The evaluation showed that the plasma enhanced the particle removal of the gas flow; namely, the combination of a down-flow plasma and a fast gas flow removed particles at an efficiency of 98% in 60 sec. It was also found that the dry scrubber produces an etching depth for poly-silicon of 0.17 nm. The cleaning capabilities of the sample with etched contact-hole patterns were also evaluated. This sample had residues of photo-resist on its surface and particles in the holes. These results confirm that the new cleaning technique can effectively removes the residues and the particles from a patterned surface. @FootnoteText@@footnote 1@Dr. K. Mosig et al., IITC2001@footnote 2@Y. Momonoi, K. Yokogawa, M. Izawa, Proc. Inter. Sym. Dry Process, (2002), p.113.

Plasma Science and Technology
Room 315 - Session PS+TF-TuM

Plasma Enchanced Chemical Vapor Deposition

Moderator: D.C. Guerin, Naval Research Laboratory

8:20am **PS+TF-TuM1 PECVD, From the Laboratory to Mass Production***, **J.P.M. Schmitt**[1],* Unaxis Management Incorporated, Switzerland **INVITED**

After a rapid recall of the "alchemist" age of gas decomposition by an electrical arc, the gradual birth of PECVD is described in the early 70's. The richness of PECVD potential was then realised creating expectations for a long list of potential applications. Soon after the first industrial applications of PECVD were demonstrated. A look back at the pioneering days of PECVD allows to identify and discuss the key attributes of PECVD that made (and keep) this technology attractive for film coating. In the early 80's PECVD was hype and was the objet of active research. Basic research teams activity focused on the complex mechanisms involved in the PECVD process. First were understood the basic steps such as electron induced molecular dissociation and particle-surface processes. It is only later that far more complex mechanisms such as dust formation were found to be also extremely important. The status of knowledge on basic mechanisms will be reviewed. In the last 15-20 years a wide variety of configurations for the plasma reactors were tested. Instead of a complete zoological classification of all variations, we relate various classes of plasmas with their most marking attributes to the PECVD process key mechanisms. If in the 80's PECVD was already at work in mass production plants, it is in the 90's that a full set of production related problems were actively addressed. Self-cleaning was found a highly desirable ability for a PECVD tool. This requirement combined with high throughput demand led to new classes of equipment and processes. The application field of PECVD also stretched from the food industry the most sophisticated high tech industry. PECVD is today facing new challenges. The glass substrate size for the flat display industry is about to exceed 2m@super 2@ still requiring good uniformity and high throughput. PECVD has also the opportunity to prove itself into new fields such as semiconductor epitaxy or deposition of organic based films with functional groups.

9:00am **PS+TF-TuM3 Plasma-enhanced Deposition of Silicon and Metal Oxynitride Films in a High-density Ammonia Discharge***, Z.G. Xiao,* ***T.D. Mantei,*** University of Cincinnati

Silicon, titanium, zirconium, and chromium oxynitride films have been grown in a high-density electron cyclotron resonance (ECR) ammonia discharge. The organosilicon deposition precursors for silicon oxynitride were hexamethyldisiloxane and tetramethylsilane, while the organometallic deposition precursors for metal oxynitride were titanium (IV) isopropoxide and tetrakis(dimethethlyamino)titanium, zirconium 2-methyl-2-butoxide and zirconium t-butoxide, and bis(ethylbenzene)chromium. The plasma-grown films had nanoindentation hardness values of 12 - 14 GPa for SiN, 20 - 28 GPa for TiN, 17 - 21 GPa for ZrN, and 25 - 31 GPa for CrN. Deposition growth rates were 40 - 50 nm/min for silicon oxynitride and 10 - 20 nm/min for the metal oxynitrides. X-ray photoelectron spectroscopic (XPS) analyses showed the nitrogen content of silicon, titanium, and zirconium oxynitrides to be 31% - 38%, while the CrN nitrogen content was 15%. The SiN films grown from hexamethyldisiloxane were colorless and transparent while films grown from tetramethylsilane had the characteristic dark color of Si@sub 3@N@sub 4@. The TiN and ZrN films had the characteristic brass and white gold colors of TiN and ZrN reference samples while the CrN samples were gray. The SiN films lasted 800 hours in an ASTM B117 accelerated salt-fog corrosion test without visible corrosion, and the TiN and ZrN films lasted 1000 hours without visible color change or corrosion.

9:20am **PS+TF-TuM4 Identification of the Growth Precursors for Hydrogenated Amorphous Carbon Growth***, **J. Benedikt**[2], R.V. Woen, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The plasma chemistry and plasma composition of argon/acetylene expanding thermal plasma, used for fast (up to 70 nm/s) hydrogenated amorphous carbon (a-C:H) film deposition, was studied by means of Cavity Ring Down absorption Spectroscopy and Mass Spectrometry. Since the electron temperature in expanding thermal plasma beam is low (less than 0.3 eV) electron impact processes can be neglected and acetylene dissociation is argon ion induced. The C@sub 2@H radical was identified as the main growth precursor for hard (14 GPa) diamond-like a-C:H films. It was shown that under conditions where most of acetylene molecules are decomposed into C, CH and C@sub 2@ radicals, the a-C:H films are soft and polymer-like. Furthermore it was observed that good a-C:H films can be grown also under conditions when C@sub 4@H@sub 2@ molecules are the main plasma chemistry product and when reactive radicals as C@sub 2@H has already reacted away with acetylene in the gas phase. The mass spectrometry measurements of C@sub 4@H@sub 2@ molecule in the background of the plasma shows that C@sub 4@H@sub 2@ density depends on the wall condition (argon plasma activated or hydrogen plasma passivated) suggesting that C@sub 4@H@sub 2@ is one of the contributors to the film growth. C@sub 2@H and C@sub 4@H@sub 2@ as possible precursors for a-C:H growth is confirmed by recent Molecular Dynamics simulations which reveal reaction probabilities close to one for both species.

9:40am **PS+TF-TuM5 Characterization of TaN Diffusion Barrier Layers Prepared by Chemical-Enhanced Physical Vapor Deposition (CEPVD)***, **N. Li**[3], D.N. Ruzic,* University of Illinois, Urbana-Champaign

CEPVD of TaN is a novel process attempting to deposit diffusion barrier layers with both high conformal step coverage (as in CVD) and superior quality (as in PVD). The experiments are performed by sputtering a Ta target in a modified conventional PVD instrument and simultaneously adding a certain amount of chemical precursor, TBTDET, in the vicinity of the substrate at elevated temperature (330@degree@C) in combination with a carrier gas (N2), reducing agent (H2), non-reactive sputtering gas (Ar) and a RF-powered secondary ionization plasma. Different combinations of RF power, N2, H2, Ar flow and bias voltage result in distinct resistivity regimes. Increasing H2 flow rate from 5 sccm to 10 sccm allows more hydrocarbon formation and thus results in significant resistivity variation. The addition of 10sccm Ar increases target sputtering and more Ta flux, producing film with relatively lower resistivity (5200 Î¼ -cm compared to 62,000 Î¼ -cm). The addition of Ar also produces a more columnar and porous structure. N2 flow rate determines precursor residence time and so controls growth density and deposition rate. Biasing the substrate with -60 V drops resistivity one order of magnitude. Patterned wafers with various trench aspect ratios are lined to compare the step coverage under different processing conditions. Four point probe, SEM, AES, XRD and XPS are utilized to characterize the film properties and the analysis reveals the balance between energetic Ta flux, TBTDET breakup and impurity volatilization. The synergy between PVD and CVD is clearly demonstrated.

10:20am **PS+TF-TuM7 Anisotropic Cu Deposition using Plasma Chemical Vapor Deposition***, **M. Shiratani**, K. Takenaka, M. Takeshita, M. Kita, K. Koga, Y. Watanabe,* Kyushu University, Japan **INVITED**

We have demonstrated complete filling of trenches by anisotropic Cu deposition, in which Cu is filled preferentially from the bottom of the trenches, using plasma chemical vapor deposition.@footnote 1@ The key to realize the anisotropic deposition is kinetic energy and flux of ions irradiating on the surface, since the deposition rate increases with increasing the kinetic energy and fluxes. Previously, by using H-assisted plasma CVD we have realized conformal deposition of smooth 20 nm thick Cu films in trenches as well as conformal filling of trenches.@footnote 2@ Although the Cu films have a low as-deposited resistivity of of 1.85 µ@ohm@cm and a strong adhesion strength above 10 MPa to the TiN layer, conformal filling results in a small crystal grain size below half of the trench width and in a seam where impurities of high concentration remain. The anisotropic deposition offers a possibility to overcome such shortcomings for the conformal filling together with two additional interesting features. One is the fact that deposition rate increases with decreasing the width of a trench. The other is a self-limiting deposition by which deposition stops automatically just after filling completely a trench. This feature may realize a LSI fabrication processes without the chemical mechanical polishing, being attractive for the Cu-porous low-k interconnects. @FootnoteText@@footnote 1@ K. Takenaka, et al., Matr. Sci. Smiconductor Processing 5, 301 (2003).@footnote 2@ M. Shiratani, et al., Sci. and Technol. of Adv. Mater. 2, 505 (2001).

[1] **AVS 50th Anniversary Invited Speaker**

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

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

11:00am **PS+TF-TuM9 Pulsed-plasma Deposition of Silicon Dioxide in a High Density Oxygen Discharge**, ***Y. Qi***, *T.D. Mantei,* University of Cincinnati

Hard clear silicon dioxide films have been grown from octamethylcyclotetrasiloxane (OMCTS) at low substrate temperatures in a pulse-modulated high density electron cyclotron resonance (ECR) oxygen plasma. The input microwave power at 2.45 GHz was pulse-modulated with repetition frequencies from 20 Hz to 20 kHz, duty ratios (on-time/period) from 5% to 100%, and peak microwave power levels from 800 W to 2400 W. The resulting films were SiO@sub 2@-like with Si-O bonds and Si:O ratios close to 1:2. The deposition growth rates were almost independent of frequency for all pulse repetition frequencies from 20 Hz to 20 kHz. The growth rates increased strongly as the peak pulse power was increased; with a 50% duty ratio, the growth rate was 0.5 - 0.6 mm/min with 800 W peak power, increasing to 0.8 - 0.9 mm/min at 1600 W peak power. The coating hardness values decreased with pulsed operation as the average input microwave power decreased. Deposition substrate temperatures were significantly lowered as the duty ratio (and thus the average power) decreased, e.g., substrate temperatures were 140°C - 150°C after 10 minutes of deposition with 1600 W of continuous microwave power, dropping to 90°C with a 50% pulse duty ratio and 1600 W peak power. Results from current experiments on pulsed low temperature growth of metal nitride and teflon coatings will also be discussed.

11:40am **PS+TF-TuM11 Secondary Plasma Based Debris Mitigation for Next-Generation 13.5nm EUVL Sources**, ***B. Jurczyk***, *D.N. Ruzic, E. Vargas-Lopez, M. Neumann, M. Williams, C. Chrpbak, S. Taj,* University of Illinois at Urbana-Champaign

Next-generation EUV photolithography machines (>25kW-class) require order of magnitude improvements in debris removal for component lifetime and stable operation. Discharge plasma light sources, such as the dense plasma focus, are leading candidates for EUV. The Illinois Debris-mitigation Experiment and Applications Laboratory (IDEAL) consists of a dense plasma focus discharge source operating on order of 25 J/pulse, 100 Hz rep rate, and 4 kV. Argon and Helium gases have been tested to generate plasma environmental conditions similar to that experienced by industry. The secondary-plasma-based debris mitigation technique is presented; a concept pioneered from iPVD reactors at the University of Illinois. Sputtered electrode and chamber component debris is re-ionized in the secondary plasma region and removed with the application of electric fields prior to the collection optics. A helical resonator inductive coil generates the secondary plasma with minimal coil self-biasing for decrease erosion. A dual-channel foil trap, with independently biased plates (0-1kV), collects debris from the secondary plasma region. The foil trap is positioned to vary aspect ratios from 1:1-to-16:1 to correlate with gas pressure effects. Results from in-situ high-precision quartz-crystal-oscillators, ex-situ surface characterization (XPS, Auger, Profilometry, etc.), secondary plasma characterization, and collection optic protection factors are presented for a series of mitigation schemes.

Plasma Science and Technology
Room 314 - Session PS-TuM

Plasma Diagnostics: Processing

Moderator: H. Sugai, Nagoya University, Japan

8:20am **PS-TuM1 Attractive Interactions Between Negatively Charged Dust Particles in a Plasma**, ***G.A. Hebner***, *M.E. Riley,* Sandia National Laboratories

Plasma dust particle interactions, charges, and screening lengths are derived from measurements of time-dependent particle positions in a simplified geometry. The magnitude and structure of the ion wakefield potential below a negatively-charged dust particle levitated in the plasma sheath region were measured as functions of the pressure and interparticle spacing. Attractive and repulsive components of the interaction force were extracted from a trajectory analysis of low-energy dust collisions between different mass particles in a well-defined electrostatic potential that constrained the dynamics of the collisions to be one dimensional. Typical peak attractions varied between 60 and 230 fN while the peak particle-particle repulsion was on the order of 60 fN. Random thermal motion of the particles contributed to observable rates for transitions between different equilibrium configurations of vertically separated particles. We also observed a slight potential barrier that impeded the formation of vertically aligned pairs. The influence of nearest- and non-nearest-neighbor interactions on calculated particle parameters are examined using several methods. Implications for plasma / surface interactions and plasma dielectric charging will be discussed. This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:40am **PS-TuM2 Measurement of Electrical Fields Around Dissimilar Materials Exposed to a Discharge**, ***E.V. Barnat***, *G.A. Hebner,* Sandia National Laboratories

The nature of a surface/plasma boundary can have an important impact on the processes that occur both in the plasma and on the bounding surface. In this work, fluorescence-dip spectroscopy is used to study the surface dependant sheath structure at the boundary of an argon glow discharge. The two laser technique monitors the variation in the fluorescence from an intermediate state caused by laser excitation from this intermediate state to Stark-shifted Rydberg levels sensitive to the electric fields present in the sheath. To demonstrate the effectiveness of the dip-spectroscopy technique, half of a conducting electrode is covered with an insulating surface and both spatially and temporally resolved measurements of the structure of the sheath are made around both the conducting and the non-conducting surfaces. The fields through the sheath above the two surfaces, the potential drops across the sheath, and the fields near the surface along the electrode are discussed for various discharge conditions. Future applications of fluorescence-dip spectroscopy will be discussed as well. @FootnoteText@ This work was supported by the Division of Material Sciences, BES, Office of Science, U. S. Department of Energy and Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. .

9:00am **PS-TuM3 Plasma Processing Diagnostic Methods and Studies: A Historical Perspective**, ***V.M. Donnelly***[1], University of Houston **INVITED**

In the late 1970's, plasma etching emerged as a breakthrough method for pattern transfer in silicon integrated circuits. Soon after, it became apparent that, to further develop this technology, it was important to understand the mechanisms responsible for anisotropic plasma etching. Researchers in industry, national laboratories and universities began applying well established diagnostic techniques, and inventing new methods, for elucidating the chemical and physical processes underlying plasma etching, as well as plasma assisted deposition. Experiments were designed to either measure parameters of the plasma (species concentrations and velocities), or to simulate plasma-surface interactions under less complex conditions (high-vacuum / beam experiments, discharge flow tubes, etc). This talk will review the history of diagnostic methods for plasma processing. An admittedly incomplete survey of plasma diagnostic techniques will begin with several methods that greatly predate the microelectronics era. Electrical, optical and beam methods will be discussed and selected key experiments will be highlighted.

9:40am **PS-TuM5 Absolute SiCl@sub X@ Densities in Silicon Gate Etching Plasmas Determined by Broad Band UV Absorption**, ***M. Kogelschatz,*** CNRS/LSP, France*; G. Cunge,* CNRS/LTM, France*; N. Sadeghi,* CNRS/LSP, France*; O. Joubert, L. Vallier,* CNRS/LTM, France

Broad band UV absorption spectroscopy has been used to measure the absolute gas phase concentration of SiCl@sub X@ and SiF@sub X@ etch products (X = 0-2) during silicon gate etching in high density HBr/Cl@sub 2@/O@sub 2@ plasmas and their mixture with fluorocarbon gases. The silicon atom concentration in the ground and metastable states has also been measured. To convert the absorption rates to the Si atom density, the instrumental width of the monochromator had to be taken into account. Typical concentrations of etch products are about 10@super 11@cm@super -3@, and their behavior with the plasma conditions (RF power, O@sub 2@ gas flow) will be discussed. Vibrationnally resolved absorption spectra of SiCl@sub 2@ and SiBr, observed for the first time in etching plasmas, will also be presented. However, due to the lack of absorption cross sections, the absolute concentration of SiBr can not be deduced. A particular emphasize will be given on correlation between these etch products and the composition of the films deposited on the plasma chamber walls. This composition was determined from the analysis by OES and mass spectrometry of products introduced in the gas phase of a weak Ar-SF6 plasma from the chamber walls. The deposit of the silicon oxychloride layers on the walls is at the origin of process drifts as it changes

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the chemical composition of the surfaces exposed to the plasma. A large change of the recombination rate of Cl atoms as a function of the reactor walls composition has been observed by measuring the variation of the Cl/Cl@sub 2@ concentration ratio in the gas phase, as well as the absolute Cl@sub 2@ concentration by UV absorption.

10:20am **PS-TuM7 In-situ Processing Memory Effects for Confined vs. Unconfined Plasmas*, E.A. Hudson*,** *R. Annapragada, D. Keil, K. Takeshita,* Lam Research Corp.

In the fabrication of integrated circuits there is a growing trend towards performing several etch steps in a single pass through an etch tool. This in-situ processing approach reduces production costs and cycle times, but presents technical challenges because it requires the sequential use of very different plasma chemistries in the same reactor. An important example is the use of a polymerizing fluorocarbon-based plasma to etch patterns into silicon dioxide or organosilicate films, followed by oxidizing plasmas to remove the remaining photoresist film. Residual fluorocarbon polymer, left on chamber surfaces by the etch step, is attacked under oxidizing conditions, releasing fluorine-containing species which may have harmful effects on the wafer structures. This paper compares the "fluorine memory" effect for unconfined vs. mechanically confined capacitively-coupled RF discharges. Diagnostic measurements focused on plasma properties, chamber surface cleaning efficiency, and wafer-level results. Optical emission spectroscopy was used to detect atomic fluorine in the plasma during the photoresist strip step. Fluorine was found to persist much longer in the case of the unconfined plasma. The impact of residual byproducts at the wafer was evaluated from silicon dioxide loss and from changes in feature dimensions. Results indicate that use of a mechanically confined plasma greatly reduces "fluorine memory" effects during the photoresist strip step, compared to the unconfined configuration. This is attributed to the reduced gas residence time and more efficient cleaning of chamber surfaces in the confined configuration.

10:40am **PS-TuM8 Plasma Diagnostics and Thin Film Characterization in Dielectric Etching: Understanding the Role of Fluorine Chemistry*, B. Ji,*** *S.A. Motika, P.R. Badowski, S. Dheandhanoo, E.J. Karwacki, J.R. Stets,* Air Products and Chemicals, Inc.*; C. Timmons, D.W. Hess,* Georgia Institute of Technology*; E.C. Benck,* National Institute of Standards and Technology*; Y. Ye,* Applied Materials, Inc.

Plasmas of fluorine-containing gases have for many years been utilized to etch dielectric materials such as silicon dioxide. Maintaining the balance between the anisotropic dielectric etch rate and formation of the protective passivation films on top of the photoresist surface and on the feature sidewalls is critical in assuring desired etch features and critical dimensions. In recent years, the semiconductor industry have adopted heavier molecular weight and lower fluorine to carbon ratio gases, such as c-C@sub 4@F@sub 8@, C@sub 5@F@sub 8@, and C@sub 4@F@sub 6@ for anisotropic dielectric etching. We performed a fundamentals study to better understand the relationship between etch gas compounds and the species formed within both capacitively and inductively coupled plasmas. UV Absorption Spectroscopy, Sub-millimeter Wave Absorption Spectroscopy, Optical Emission Spectroscopy, Mass Spectrometry, and X-ray Photoelectron Spectroscopy were employed to evaluate the gas phase and surface chemistries of these three etching molecules.

11:00am **PS-TuM9 Loss Kinetics of CF@sub x@ Radicals and F Atoms in the Afterglow of Inductively Coupled Pulsed Plasmas*, X. Wu,*** *J.L. Cecchi,* University of New Mexico

We have studied the time evolution of the concentrations of CF, CF@sub 2@, and F in inductively coupled pulsed (ICP) plasmas after the termination of the discharge. The feed gases included CHF@sub 3@ and C@sub 2@F@sub 6@, with additions of H@sub 2@and O@sub 2@, to vary the amount of radicals and F produced in the discharge. Our observations were made over the pressure range from 10 to 60 mTorr and for inductively coupled powers of 300 to 900 W. Concentrations were determined by time-resolved wavelength modulated diode laser absorption spectroscopy for the radicals and by time-resolved actinometry for F. The latter measurements were facilitated by maintaining a small amount of power on the wafer chuck after the termination of the ICP power pulse. CF and F both exhibited first order exponential decays. The decay rates of CF increased with increasing pressure, suggesting the presence of gas phase loss processes in addition to losses at surfaces. The decay rates of CF varied linearly with F concentration, indicating that the gas phase reaction is likely due to the recombination with F atoms. CF@sub 2@ exhibited second-order decay. Possible mechanisms for this will be discussed.

11:20am **PS-TuM10 Effect of an Applied-phase of Bias Pulse on a Charge Reduction on a SiO@sub 2@ Hole Exposed to Plasma Etching in a Two-frequency CCP*, T. Ohmori*,** *T.K. Goto, T. Makabe,* Keio University, Japan

In a top-down nano-meter scale etching, it will be essential to develop in-situ diagnostics for plasma damage in the interface under close and complementary cooperation between optical and electric procedure. In our previous paper@footnote 1@ we have applied an emission selected computerized tomography close to the wafer exposed to plasma etching, in order to investigate the polarity and the phase of high energy charged particles incident on the wafer deeply biased by a low frequency source in RIE. A reduction in charging voltage on a contact hole bottom of SiO@sub 2@ was measured in the pulsed plasma power source in the 2f-CCP in CF@sub 4@/Ar by using a dual measurement system consisting of a temporal emission CT and a contact hole charging. In the present work, detailed correlational results of the reduction in the charging voltage are shown as a function of phase and amplitude of the single bias pulse at 500 kHz. Discussion is focused both on the injection mechanism of energetic negative charges to the wafer and on the magnitude of the negative charges. As a result, during the off-period 10 µs of VHF power source it is confirmed in the present pulsed 2f-CCP system that:(1)the magnitude of the injected negative charge increases with increasing the threshold time of the single bias pulse, and at the same time a strong reduction in the charging voltage is performed, (2)secondary a strong negative self-bias-voltage is always kept to have an efficient RIE with energetic positive ions on the wafer except for the period of the single bias pulse. @FootnoteText@ @footnote 1@T.Ohmori, T.K.Goto, T.Kitajima, and T.Makabe, Proc.of Dry Process Symposium 165(2002)Tokyo, Appl.Phys.Lett.(submitted).

11:40am **PS-TuM11 Analysis of Downstream Etch Chemistry in Ion-Ion and Electron-Ion Cl2 Discharges*, A.K. Jindal,*** *A.J. Prengler, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

It has been shown that ion-ion plasmas can significantly reduce substrate charging damage. This study clearly shows that ion-ion plasmas also influence the etch chemistry. This knowledge may facilitate improvements in plasma processing or environmental control. Here, we use FTIR spectroscopy to examine the volatile etch products downstream of the turbo pump resulting from the etching of C-Si, SiO2, and photoresist in electron-ion and ion-ion Cl2 discharges. RF power is either pulsed to produce ion-ion plasmas or continuous to produce electron-ion plasmas. An independently controlled chuck is rf biased to produce an alternating flux of negative and positive ions or a combination of electrons, negative ions, and positive ions at the substrate. Changes in etch chemistry are studied and compared as functions of biasing schemes and substrate chuck voltages. Continuous wave (electron-ion), asynchronous, and synchronous, biasing regimes are all subjected to peak to peak chuck biases of 25, 50, 75, and 100 V via a 300 kHz waveform. Asynchronous and synchronous (ion-ion) modes apply to 1 kHz, 50 percent duty ratio pulsed regimes of the discharge in which the former implies continuous biasing throughout the entire pulse cycle and the latter to only the afterglow, where an ion-ion plasma exists. Clear distinctions in etch chemistry are evident solely based upon the biasing scheme. For example, CO2 is observed for all chuck biases in both pulsed regimes during photoresist etch, but no signal is apparent at lower biases in the continuous mode. Not only is there an undeniable difference in etch chemistry, but we can affect our emission by varying the biasing scheme. This work was funded in part by a grant from NSF/DOE, contract number CTS-0078669 and a grant from NSF, contract number CTS-0079783.

Plasma Science and Technology
Room 315 - Session PS-TuA

Dielectric Etch

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

2:00pm **PS-TuA1 Dielectric Etch: Past, Present and Future***, **T.J. Dalton**[1],* IBM Research **INVITED**

Dielectric etch has grown in importance during the last decade with the emergence of single- and dual-damascene processing for semiconductor interconnect structures utilizing copper metallurgy, first in research and development and now in high-volume manufacturing. At the same time, the challenges of dielectric etch for semiconductor processing have changed significantly due to two factors. First, the materials of interest have evolved from silicon dioxide to "dense" low dielectric constant ("low-k") materials (both organic and silicate) to porous low-k materials (again, both organic and silicate). Second, the critical dimension (CD) has decreased to the sub 100-nm regime, forcing extreme control of feature sizes and sidewall profiles. This talk will focus on the evolution of dielectric etch for advanced logic integrated circuit fabrication in the last decade, specifically discussing dielectric materials, etch processes, and etching sources. Additionally, we will look ahead to issues with dielectric etch in the future.

2:40pm **PS-TuA3 Depth Dependent Spatial Frequency Analysis of Post-Etch Sidewall Roughness***, **S.A. Rasgon**, H.H. Sawin,* Massachusetts Institute of Technology*; A.P. Mahorowala, D. Goldfarb, M. Angelopoulos,* IBM T.J. Watson Research Center*; S.D. Allen,* IBM Microelectronics Division

For the patterning of sub-100 nm features, a clear understanding of the origin and control of line edge roughness (LER) is extremely desirable. Until recently, LER studies have focused on the analysis of top-down SEM micrographs of post-developed photoresist lines. However, plasma etching processes often roughen the feature sidewalls and might form striations. This post-etch substrate LER is probably more relevant from a manufacturing perspective than the post-developed LER. The depth dependence of the post-etch sidewall morphology cannot be captured adequately by top down SEM techniques. A novel atomic force microscopy (AFM) technique developed by Reynolds and Taylor (JVST B 17(2), p. 334-344, 1999) was used to examine sidewall roughness (SWR) transfer through photoresist, BARC/hardmask, and oxide layers simultaneously. Dense line-and-space structures were cleaved parallel to the line patterns, and turned 90 degrees to access the exposed sidewall with the AFM tip. The images vividly highlight the resulting SWR structure, allowing one to observe roughness transfer through materials and determine any potential correlations. This paper studies the effect of etch chemistry, BARC/hardmask material, and resist thickness/type on the morphology and structure of SWR striation spatial frequency and spatial correlation, under conditions typically encountered during oxide etch processes. Quantitative data on RMS roughness and striation spatial frequency as a function of feature depth is collected using AFM-based techniques. Power spectral density (PSD) and correlation analysis of the sidewall AFM images allows us to track the evolution of sidewall striations through the various feature layers after each process step (lithography, BARC/hardmask open, and oxide etch). Finally, the impact of these sidewall striations on future processing steps (for instance, conformal liner deposition) is discussed.

3:00pm **PS-TuA4 Investigation of Bottom-emitted Particles and their Influence on the Etch Characteristics of Sidewall in the Fluorocarbon Plasma Etching***, **G.-R. Lee**, J.-H. Min, J.-K. Lee, S.H. Moon,* Seoul National University, Korea

When energetic ions impinge on the bottom of an etched pattern, various particles are emitted from the bottom surface, which constitute an additional source for modifying the composition of plasma gases besides collisions among gas-phase particles generated in a plasma. The effect of bottom-emitted particles on the composition of gas-phase radicals increases with a decrease in the distance from the bottom surface and, accordingly, the etch characteristics of sidewalls in proximity to the bottom of an etched pattern is strongly affected by the bottom-emitted particles. However, information about the bottom-emitted particles, including species and amount of the particles and their influence on the etch characteristics of sidewall, is limited largely due to the lack of experimental methods for observing the phenomenon in a larger scale. In this study, we have analyzed particles emitted from different bottom materials using mass spectrometry at various bias voltages. We also examined the effect of the bottom-emitted particles on the etch characteristics of a SiO@sub 2@ surface located vertically and in proximity to the bottom surface. Ions of high energy sputter the steady-state fluorocarbon polymer layer covering the bottom to generate heavy and unsaturated fluorocarbon radicals, which contribute to the etch characteristics of the sidewall. As a result, the effect of bottom-emitted particles on the sidewall etching is profound under the conditions of high bias voltages and those allowing the formation of a thick steady-state polymer layer on the bottom surface.

3:20pm **PS-TuA5 Bilayer Mask Process for sub-90 nm Patterning using a New 100MHz CCP RIE***, **H. Hayashi**, J. Abe, A. Kojima, J. Nishiwaki, A. Takase, K. Sho, E. Shiobara, I. Sakai, E. Shinomiya, T. Ohiwa,* TOSHIBA Corporation Semiconductor Company, Japan

Shrinkage of LSI design rule, especially to sub-90 nm nodes, necessitates the reduction of photoresist thickness to maintain the process window in deep UV lithography. However, thinning the resist layer leads to critical dimension (CD) loss in the subsequent etch process due to resist erosion. A bilayer mask process, in which patterns formed at the Si-containing resist layer are transferred to spun-on-carbon film having anti-reflective property, is a promising candidate for sub-90 nm patterning. However, this process can be used only if carbon film etching with high selectivity to the thin Si-containing ArF resist is realized. In this paper, a new reactive ion etching (RIE) employing 100 MHz capacitive coupled plasma (CCP) where the wafer is placed on the cathode, is proposed. By introducing the high frequency of 100 MHz, low ion energy and high selectivity could be expected. Self-bias voltages (Vdc) generated in the 100 MHz Ar plasma at 40 mTorr were 20 to 90 V depending on RF power, less than 1/3 those of the 13.56 MHz plasma which were 290 to 540 V under the same conditions. As a result, the carbon film etch process using the 100 MHz plasma in hydrogen based gas chemistry showed great improvement of selectivity, to more than 8. Etch rates of the carbon film were 200 to 300 nm/min at the pressures of 5 to 100 mTorr. Finally, the etch profile of a pattern with a resist thickness of 150 nm and carbon 300 nm thick was examined, and it was found that a vertical carbon etch profile was obtained, with less faceting of the Si-containing resist mask. The ArF bilayer mask process combined with the new 100 MHz CCP proves to be the most effective patterning process for devices of 90 nm and below.

3:40pm **PS-TuA6 Etching Bilayer Resists in Ammonia Based Plasmas***, **S. Panda**, R. Wise, A.P. Mahorowala,* IBM

Bilayer resist schemes (thin, silicon containing image layer over thick, organic transfer layer) can mitigate lithographic limitations associated with the smaller wavelengths and higher NA values required for patterning shrinking feature sizes. State of the art transfer etch processes utilize an oxygen based chemistry to oxidize Si in the image layer while etching the transfer layer beneath. Undercutting of the image layer, poor CD control, and LER can result from the use of oxidizing chemistry, and are exacerbated by more sensitive ArF materials. Commonly used SO2 addition (for sidewall passivation) can form undesirable byproducts leading to both tool and line contamination. In the present study we present an oxygen-free ammonia based transfer etch process. In addition to NH@sub3@; N@sub2@, H@sub2@, and C@sub2@H@sub4@ were examined as additives. It is hypothesized that selectivity to the underlayer arises from nitridation of the silicon containing image layer which becomes resistant to etch. XPS analyses of the etched samples, optical emission and mass spectroscopic studies were performed to understand the mechanisms involved.

4:00pm **PS-TuA7 Model for Dielectric Etching in C@sub 4@F@sub 6@ Based Inductively Coupled and Dual Frequency Plasmas***, **S. Rauf**, P.J. Stout, P. Ventzek,* Motorola Semiconductor Products Sector*; S. Adamson, A. Dementev, K. Novoselov, V. Kudrja,* Soft-Tec, Moscow, Russia

1,3 Perfluorobutadiene (C@sub 4@F@sub 6@) has recently received much attention in the microelectronics industry for etching of conventional and low-@kappa@ dielectrics. This consideration is motivated in part due to the environmentally benign nature of C@sub 4@F@sub 6@, and its desirable etching and polymerizing characteristics. This paper describes a model for etching of SiO@sub 2@ and Si in medium and high density Ar/C@sub 4@F@sub 6@/O@sub 2@ plasmas. The plasma chemical mechanism for C@sub 4@F@sub 6@ is assembled using measured dissociative ionization and attachment cross-sections, and first principle based computations of C@sub 4@F@sub 6@ neutral dissociation kinetics and cross-sections. The plasma surface interaction mechanism has been constructed empirically by correlating computed species characteristics with experimentally measured etching and deposition rates. Computational

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modeling of the plasma and surface processes is conducted using a combination of 2-dimensional plasma equipment models (HPEM@footnote 1@ from University of Illinois and IO)@footnote 2@ and feature scale simulations (BabyBean@footnote 3@ and Papaya).@footnote 4@ The paper discusses experimental validation of the model in two disparate plasma operating regimes, ICP@footnote 5@ and dual frequency.@footnote 6@ The model is also used to understand the differences in plasma chemistry of medium and high density C@sub 4@F@sub 6@ based plasmas, and how these differences impact dielectric etching characteristics. @FootnoteText@ @footnote 1@P. L. G. Ventzek et al., J. Vac. Sci. Technol. B 12, 461 (1994)@footnote 2@S. Rauf, to appear in IEEE Trans. Plasma Sci. (Aug. 2003)@footnote 3@S. Rauf et al., J. Vac. Sci. Technol. A 20, 1177 (2002)@footnote 4@P. J. Stout et al., J. Vac. Sci. Technol. A 21, 265 (2003)@footnote 5@X. Li et al., J. Vac. Sci. Technol. A 20, 2052 (2002)@footnote 6@F. Fracassi et al., J. Vac. Sci. Technol. A 21, 638 (2003).

4:20pm **PS-TuA8 A Computational Investigation of Plasma and Surface Chemistry During Fluorocarbon Plasma Etching of SiO@sub 2@ in Ar/c-C@sub 4@F@sub 8@/O@sub 2@/CO Magnetically Enhanced Capacitively and Inductively Coupled Plasmas@footnote 1@**, ***A.V. Vasenkov****, M.J. Kushner,* University of Illinois at Urbana-Champaign

Gas mixtures containing Ar, c-C@sub 4@F@sub 8@, O@sub 2@, O@sub 2@, and CO are often used for the plasma etching of silicon dioxide in order to optimize the fluxes of etching, polymerizing and activating species to the substrate. Reaction mechanisms, both gas phase and surface, are required for first principle modeling of these systems to both provide insights to the plasma chemistry and to help optimize the process. In this paper, we describe a refined gas-phase reaction mechanism for low-pressure and low-temperature plasmas sustained in mixtures initially consisting of Ar/c-C@sub 4@F@sub 8@/O@sub 2@/CO/N@sub 2@ or any combination, and its application to a computational investigation of plasma properties in magnetically enhanced inductively coupled plasmas (MEICPs) and magnetically enhanced capacitively coupled plasmas (MECCPs, or MERIEs). The systemmatic dependence of ion and radical fluxes, and ion energy distributions on gas mixtures, power and pressure will be discussed. Comparisons will be made between MEICPs and MECCPs. Predictions for ion saturation current were compared to experiments MEICPs sustained in Ar/c-C@sub 4@F@sub 8@ and O@sub 2@/c-C@sub 4@F@sub 8@ for validation. Principle differences between MEICPs and MERIES is the average molecular weight of both the radicals and ions, being higher in MERIES. @FootnoteText@ @footnote 1@ Work supported by Semiconductor Research Corporation, SEMATECH and the National Science Foundation.

4:40pm **PS-TuA9 Kinetic Study on SiO@sub 2@ Dry Etching Process by Chemical Reaction Engineering Approach***, **T. Tokimitsu**, Y. Shimogaki,* University of Tokyo, Japan

Kinetic study on plasma process to etch SiO@sub 2@ films using C@sub 4@F@sub 8@ was made by chemical reaction engineering approach. In the present study, we assumed that the reactor as a CSTR (continuously stirred tank reactor) and examined the residence time dependency of gaseous species concentration. This approach is quite effective to elucidate the reaction mechanism that governs the performance of plasma reactor. Ionization voltage controlled AMS (appearance mass spectrometry) was conducted and it was found to be possible to measure the absolute concentration of each molecule. The residence time dependency of C@sub 4@F@sub 8@, C@sub 2@F@sub 4@ and C@sub 2@F@sub 6@ concentrations were measured by this technique. It was found that the main species in plasma changed from C@sub 4@F@sub 8@ to C@sub 2@F@sub 4@, and finally changed into C@sub 2@F@sub 6@ as residence time gets longer. C@sub 2@F@sub 4@, whose residence time dependency had a bowed profile, was the species to deposit a-C:F films and to prevent SiO@sub 2@ etching. O@sub 2@ addition to this plasma chemistry accelerate the decomposition of C@sub 4@F@sub 8@ and suppresses the C@sub 2@F@sub 4@ concentration. The residence time dependency of etching profiles were examined and discussed. Moreover, to investigate the surface reaction of SiO@sub 2@ etching, test structure was employed to make detail analysis through feature scale study. The gas phase analysis made by AMS method and the measurement of residence time dependency of each species concentration combined with feature scale analysis were sensitive tool to understand the major reaction path.

5:00pm **PS-TuA10 Selective Silicon Nitride Etching by ECR Plasmas Using SF6 and NF3 Based Gas Mixtures**, *C. Reyes-Betanzo,* INAOE- Instituto Nacional de Astrofisica, Mexico*; S.A. Moshkalyov, A.C.S. Ramos,* ***J.W. Swart****,* UNICAMP, Brazil

Removal of silicon nitride films is critical step in CMOS and other semiconductor technologies as possible overetch during the nitride layer processing may result in damages of a thin oxide or a silicon substrate. Hence high nitride etching selectivity over oxide and Si is required. In recent chemical dry etching experiments, mixtures rich in oxygen and nitrogen with small additions of fluorine containing gases were shown to etch the nitride selectively. The role of NO molecules in the surface chemistry was shown to be important for improvement of the etching selectivity. This is attributed to an exothermic reaction of NO molecules with surface nitrogen atoms which promotes the enhanced removal of nitrogen (in a molecular form) from the nitride surface and thus accelerates the overall reaction rate. Here, the results of a study of silicon nitride, oxide and Si etching in SF6 and NF3 based mixtures using a high-density ECR plasma are presented. For the two fluorine containing gases used, the main mechanisms responsible for selective nitride etching are distinctly different. In the SF6 case, best results are achieved in O2/N2 rich plasmas where the nitride etching by fluorine can be enhanced by NO molecules produced in gas phase reactions. Formation of NO molecules was observed in spectra emitted from the plasma. In NF3 based mixtures, the nitride etching is more likely to be dominated by NFx reaction intermediates rather than by NO radicals. Higher selectivities over oxide (up to 100) were obtained with NF3 , while higher selectivities over Si (up to 10) were obtained with SF6 based mixtures.

Plasma Science and Technology
Room Hall A-C - Session PS-TuP
Poster Session

PS-TuP1 Silicon Dioxide Etching Processes Employing Electron Beam Excited Plasmas*, M. Ito*, *K. Takeda, Y. Tomekawa, M. Iwawaki, T. Shiina, Y. Okamura,* Wakayama University, Japan*; M. Hori, T. Goto,* Nagoya University, Japan

Optical devices or micro total analysis system fabricated by using micromachining techniques attract much attention because of their usefulness. In the fabrication processes, micromachinings of non-planer thick dielectric materials such as optical fibers and thick quartz parts are necessary. In such processes, the fast atomic beam etching and ion beam etching are employed because the RF self-biasing in the conventional reactive ion etching (RIE) is not applicable to non-planer dielectric materials such as silicon dioxide (SiO@sub 2@). However, the etch rates of these processes are typically around few tens nm/min, which are very low compared with the RIE and so the higher etch rate is strongly required to reduce the processing time. Therefore, the biasing effect is necessary to etch the SiO@sub 2@. On the other hand, an electron beam excited plasma (EBEP) has an excellent potential for applying self-bias to the non-planer dielectrics by using the electron beam. The SiO@sub 2@ etching characteristics using EBEP have been never reported although the SiO@sub 2@ is useful for the devices using micromachining techniques. Therefore, we have demonstrated the SiO@sub 2@ etching processes using self-biasing induced by an electron beam of the EBEP without any additional bias power supply. As a source gas, the CF@sub 4@ diluted by Ar (CF@sub 4@/Ar) was employed. The etch rate of 117 nm/min has been obtained. From the plasma diagnostics using a Langmuir probe and an optical emission spectroscopy, it has been found that the higher electron beam current for generating plasmas improves the plasma density and sheath potential, resulting in higher etch rate of SiO@sub 2@. Moreover, novel pulsed EBEPs have been applied for the SiO@sub 2@ etching process. The plasma diagnostics have been carried out. These results indicated that the electron beam excited plasmas has a great potential for application to micromachining processes.

PS-TuP2 A Novel Si/SiO@sub 2@ Etching Technique for Minimizing Charge-induced Microscopic Non-uniformity in Plasma Etching*, K.H. Baek,* Samsung Electronics, South Korea*; D.H. Lee, S.J. Jung,* Sungkyunkwan University, South Korea*; C.J. Kang,* Samsung Electronics, South Korea, Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

In this study, microscopic non-uniform etching characteristics solely caused by positive ions were investigated and a novel etching technique using energetic and directional neutrals was introduced as an alternative of reducing those charge-induced phenomena. To systematically investigate microscopic non-uniform etching characteristics, various samples designed to evaluate microscopic etching characteristics were prepared and etched in a homemade ICP(inductively coupled plasma) etching system, ion beam etching system, and neutral beam etching system. By analyzing all the results, we could clarify role of positive ions in the non-uniform etching phenomena and get an idea on reducing them. To realize the idea, we revised our previous neutral beam etching system so that it could improve flux and directionality of neutrals. By using this system, successful etching results for poly-Si and SiO2 nearly without the charge-induced phenomena were achieved, even though the results etched in the other systems show those non-uniform etching characteristics. Thus, we recommend energetic and directional neutrals as a potential etching source for the next generation technology era.

PS-TuP3 Effects of Substrate Temperature and Ultraviolet Radiation on the Etching of Copper Films using Inductively Coupled Chlorine-based Plasmas*, K.H. Jang,* Sungkyunkwan University, South Korea*; H.R. Kim, W.J. Lee,* IMG, LG-Production Engineering Research Center*; G.Y. Yeom,* Sungkyunkwan University, South Korea

Copper(Cu) is one of the potential materials in thin film transistor liquid crystal display (TFT-LCD) because of its lower bulk resistivity and lower cost than aluminium alloy, chromium, tungsten, and nickel at room temperature. Cu etching for TFT-LCD is currently performed using wet etching methods, however, for the fabrication of high resolution display devices, the use of plasma etching process is indispensable. In reality there are several problems to be solved before Cu plasma etching to be applied to TFT-LCD processing. The main problems are the formation of involatile etch products, lower etch rates, and high surface roughness after removing the etch products. For example, many works on Cu etching using chlorine-based plasma have been studied, however, slow etch rates and thick involatile Cu etch products remaining during the etching were reported especially for the integrated circuit (IC) manufacturing. Therefore, in this study, using an inductively coupled chlorine-based plasma, the effects of substrate temperature and ultraviolet radiation effects were investigated to obtain Cu etch rates higher than 200 nm/min and to remove the involatile etch products by changing substrate temperature and ultraviolet photon density and strength. To understand the Cu etching characteristics, we used the optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) and measured the substrate temperature and ultraviolet intensity and wavelength. Also, a scanning electron microscope (SEM) was used to observe etched Cu electrodes profile.

PS-TuP4 The Electrical Properties of SBT Thin Films Etched in BCl@sub 3@/Cl@sub 2@/Ar Plasma*, J.K. Kim, C.I. Kim, K.T. Kim, D.P. Kim,* Chung-Ang University, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) thin films have a lot of good features such as high resistance to polarization fatigue due to the charge-compensating role of the (Bi@sub 2@O@sub 2@)@super 2+@. The 200-nm SBT thin films were deposited on the Pt electrode by metal organic deposition (MOD). Until now, there is no report on the etching characteristics of SBT thin films in BCl@sub 3@/Cl@sub 2@/Ar inductively coupled plasma (ICP). Therefore, SBT thin films were etched in BCl@sub 3@/Cl@sub 2@/Ar with using ICP etching system. The etch rates and selectivity of SBT thin films were investigated as functions of gas mixing ratio, rf power, dc-bias voltage and pressure. With adding 20% BCl@sub 3@ in Cl@sub 2@/Ar plasma, increasing rf power and dc bias voltage, and lowering pressure, the etch rate of SBT increased. The etching byproducts were investigated with using quadruple mass spectroscopy (QMS). The heterogeneous reaction of plasma on the surface of the etched SBT was investigated with x-ray photoelectron spectroscopy (XPS). The etching profiles of samples have been investigated with using scanning electron microscopy. The chemical states on the etched surface were investigated with XPS. After the etching, the electrical properties of SBT capacitors were characterized in terms of hysteresis curves, leakage current and switching polarization. After etching in BCl@sub 3@/Cl@sub 2@/Ar plasma, the remanent polarization decreased and the leakage current increased. After the annealing at 600°C in an O@sub 2@ atmosphere for 10 min, the ferroelectric properties were significantly recovered. The degradation of electrical properties after the etching was considered due to the physical effect of ion bombardment and chemical residue contamination.

PS-TuP5 Modeling of Etching Mechanism of PZT in Cl@sub 2@ Plasma with the Addition of Ar, O@sub 2@*, S.M. Koo, C.I. Kim, D.P. Kim, K.T. Kim,* Chung-Ang University, Korea

Ferroelectric Lead Zirconate Titanate (Pb(Zr,Ti)O@sub 3@) thin films have been widely known as capacitor materials in nonvolatile ferroelecric random access memory (FRAM). the desirable properties such as high permittivity, high remnant polarization, fast switching speed, high Curie point and resistivity. Now, 32Mbit FRAM has been developed and some companies attempt to use FRAM as mobile phone memory. But the larger FRAM capacity, the smaller feature size. Therefore, in order to accomplish the integration of such devices, the etching process of PZT thin films with high etch rate, vertical etch profile, low by-product must be developed. PZT thin films were prepared on Pt/Ti/SiO@sub 2@/Si substrates by sol-gel processes. Pt top electrodes were deposited on PZT thin films by using rf magnetron sputtering. SiO@sub 2@ was deposited on Pt top electrodes. SiO@sub 2@ layer was etched in CF@sub 4@/Ar inductively coupled plasma with PR mask. We continued etching Pt/PZT/Pt layer without removing PR and SiO@sub 2@ patterns. PZT thin films were etched with two steps. First, it was etched with Cl@sub 2@/Ar inductively coupled plasma, then instead of Ar, it added O@sub 2@ to Cl@sub 2@ plasma. We observed the effect of etching profile in PZT thin films during etching in Cl@sub 2@/Ar, Cl@sub 2@/O@sub 2@ 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@sub 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 x-ray diffraction (XRD). The chemical deformation of etched surface was surveyed x-ray photoelectron spectroscopy (XPS).

PS-TuP6 Etching Characteristics of LNO (LaNiO@sub 3@) Thin Films Using Inductively Coupled Plasma*, C.I. Kim,* ***J.W. Yeo****, K.T. Kim, D.P. Kim,* Chung-Ang University, Korea

Among the ferroelectric thin films that have been widely investigated for ferroelectric random access memory (FRAM) application, the LaNiO@sub 3@ (LNO) thin film is known to play a role to improve fatigue and imprint of ferroelectric capacitor. And LNO thin film is expected as an effective electrode for the growth of highly oriented ferroelectric thin films because it shows a pseudocubic perovskite structure (a = 3.84 Å) and an n-type metallic behavior without any doping procedure. Although, there are several advantages and Dry etching, which shows anisotropic etching properties, has become one of the critical processes for pattern transfer in ultra large scale integration, very few studies on the etch properties of LNO electrode thin films have been reported. In this study, LNO thin films were etched by BCl@sub 3@/Ar plasma with inductively coupled plasma etching system. The etch rates of LNO thin films and selectivity of LNO to SiO@sub 2@ were investigated as functions of gas mixing ratio, rf power, dc-bias voltage, pressure and gas flow. To understand the effects of etching parameters, the atoms of B, Cl and the ions of Ar were investigated in BCl@sub 3@/Ar plasma using optical emission spectroscopy and Langmuir probe. The etching byproducts were investigated with using quadruple mass spectroscopy. The heterogeneous reaction of plasma on the surface of the etched LNO was investigated with x-ray photoeletron spectroscopy and secondary ion mass spectroscopy. The etching profiles of samples have been investigated with scanning electron microscopy.

PS-TuP7 Plasma Etching of Cantilever Epitaxy Sapphire Substrates*,* ***K.C. Cross****, K.H.A. Bogart, C.C. Mitchell, R.D. Briggs,* Sandia National Laboratories

Growth of GaN-based wide bandgap semiconductors by MOCVD is performed on sapphire, silicon carbide, or silicon substrates due to the lack of bulk crystalline GaN. Cantilever epitaxy (CE), a new lateral overgrowth method, utilizes sapphire substrates patterned by plasma etching. CE is advantageous because it requires only one growth run to achieve <5E7 dislocations per cm@super2@, nearly one to two orders of magnitude lower than standard planar growth. The sapphire (Al@sub2@O@sub3@) material is exceedingly difficult to etch due to the large Al-O bond strength (122.4 kcal/mol). We have developed a method for plasma etching of sapphire. The etching mask for the sapphire is a quad-level film stack consisting of a release layer, hardbaked photoresist, silicon nitride, and imaging resist, and is etched in an ECR plasma with O@sub2@/Ar chemistry. The sapphire is etched in an ICP system with high rf source and substrate powers, low pressure and temperature, and chlorine-based chemistry. Typical etching rates are 580 Å/min with a selectivity of 0.3, for etch depths of 2-4 µm. Issues that have been difficult to overcome include etch uniformity over 50 mm, critical dimension control, and profile control. Data and optimization of the etching process will be presented. Results from experiments to characterize the etching process as a function of rf source power, substrate bias, pressure, temperature, and gas chemistry will also be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

PS-TuP8 Effect of O@sub 2@/Cl@sub 2@ Gas Mixing Ratio on Dry Etching Characteristics and Electrical Properties of Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ Films*,* ***D.P. Kim****, C.I. Kim, K.T. Kim,* Chung-Ang University, Korea*; A.M. Efremov,* Ivanovo State University of Chemistry and Technology, Russia

Recently, Bi@sub 4-x@La@sub x@Ti@sub 3@O@sub 12@ (BLT) has been considered a predominant candidates for ferroelectric random access memory because of its high resistance to polarization fatigue due to Bi@sub 2@O@sub 2@ layers, which reduce space charges and the unpinning of domain walls. There are a lot of reports on deposition BLT thin films, but there is no report on the etching characteristics and electrical properties of BLT in Cl@sub 2@/O@sub 2@ plasma. The BLT of 200 nm was spun-coated on a Pt/Ti/SiO@sub 2@/Si substrate by MOD. Pt thin films, which used as top electrode, were deposited on BLT. BLT thin films were etched in Cl@sub 2@/O@sub 2@ using ICP because it is easy to control energy of infringing ions to the substrate. When Cl@sub 2@-based gas mixtures were used with Ar and O@sub 2@, the etch products remaining on the substrate could be observed after etching because of their very low vapor pressure. The etch rates and selectivity of BLT thin films were investigated as a function of gas mixing ratio, rf power, dc-bias voltage, and pressure. With adding 20 % O@sub 2@ in Cl@sub 2@ plasma, increasing rf power and dc bias voltage and lowering pressure, the etch rate of BLT increased. To understand the effects of etching parameters on the etch rates of BLT thin films, the atoms of Cl and O investigated using optical emission spectroscopy and Langmuir probe. The surface of the etched BLT was investigated with x-ray photoelectron spectroscopy. To estimate electrical properties of BLT after etching process, the etched species were characterized with measuring leakage current using semiconductor parameter analyzer [HP4145B] and P-E loops of Pt/BLT/Pt capacitor using precision work station. In Cl@sub 2@/O@sub 2@ plasma, we obtained higher low remnant polarization value and lower leakage current density compared with Cl@sub 2@/Ar plasma. @FootnoteText@ Acknowledgement: This work was supported by grant No. R01-2001-00268 from the Korea Science & Engineering Foundation.

PS-TuP10 Production of Electron-Temperature-Controllable ECR Plasma for Thin Film Deposition*,* ***N. Itagaki****, H. Muta,* Kyushu University, Japan*; N. Ishii,* Tokyo Electron Co. Ltd., Japan*; Y. Kawai,* Kyushu University, Japan

In semiconductor processing, it is required to control the electron temperature (T@sub e@) in the plasma for progress of microelectronic devices and minimization of substrate damage. An electron cyclotron resonance (ECR) plasma source has attracted much attention for its high electron density that can be achieved at low gas pressure. However, in a conventional ECR plasma produced by 2.45 GHz microwave, T@sub e@ is relatively high and quite hard to be controlled in a wide range. Recently, we have clarified that T@sub e@ in a 915 MHz ECR plasma depends on the spatial profiles of the microwave power absorption by both the measurement of electromagnetic waves and the calculation of microwave power absorptions. Since the power absorption profile is influenced by the effective resonance zone width (@DELTA@z@sub res@, above-mentioned results implies that T@sub e@ can be controlled by varying @DELTA@z@sub res@ which is determined from the magnetic field gradient and the microwave frequency. In this report, the spatial profiles of wave patterns were measured at different @DELTA@z@sub res@ to make clear the relationship between the power absorption profiles and @DELTA@z@sub res@. Furthermore, we tried to control T@sub e@ by changing the magnetic field gradient in order to examine whether or not the above-mentioned way to control T@sub e@ is an effective method. As a result, the power absorption profiles were confirmed to change with @DELTA@z@sub res@, which indicated that T@sub e@ could be controlled by varying @DELTA@z@sub res@. In fact, we observed that T@sub e@ varied from 1.9 eV up to 3.5 eV with increasing the magnetic field gradient at the resonance point from 0.3 G/mm to 1.4 G/mm for N@sub 2@ plasma. The experiments on thin film deposition were also performed to investigate the relationship between T@sub e@ in the plasma and the quality of prepared films, which will be presented at the conference.

PS-TuP11 Fabrication of Carbon Nanowalls Using RF Plasma-Enhanced Chemical Vapor Deposition Assisted by Hydrogen Radical Injection@footnote 1@*,* ***K. Shiji****, M. Hiramatsu, T. Kadoya, H. Amano, Y. Ando,* Meijo University, Japan*; M. Hori,* Nagoya University, Japan

Carbon nanostructures are of tremendous interest from both a fundamental and an applied prospective. Recently, fabrication of two-dimensional carbon nanostructures (carbon nanowalls) was reported.@footnote 2@ The large surface area of carbon nanowalls may provide us various new applications. In the case of film formation using plasma-enhanced chemical vapor deposition (PECVD) technique, surface morphology can be effectively controlled not only by optimizing the substrate temperature and bias, but also by the inclusion of specific reactive species as appropriate to the film growth and nucleation. Previously we demonstrated the diamond growth using a unique PECVD system that consists of a parallel-plate radio-frequency (rf, 13.56 MHz) capacitively coupled plasma (CCP) assisted by a hydrogen (H) radical source.@footnote 3@ In this work, carbon nanowalls were successfully fabricated on silicon (Si) substrate using C@sub 2@F@sub 6@ rf-CCP assisted by H radical injection from H@sub 2@ inductively coupled plasma (ICP). Partial pressures of C@sub 2@F@sub 6@ and H@sub 2@ were 20 and 80 mTorr, respectively, and the total pressure was 100 mTorr. The rf powers of CCP and ICP were 100 and 400 W, respectively, and the substrate temperature was 500 °C. Growth experiments were conducted for 2 hours. Carbon nanowalls were grown vertically on the Si substrate without catalyst. The thickness of these carbon nanowalls grown was 10-30 nm, and their height was about 300 nm. The aggregation of carbon nanowalls would be useful as templates for the fabrication of other types of nanostructured materials. In the case of the deposition without ICP, on the other hand, carbon nanowalls were not fabricated. @FootnoteText@ @footnote 1@This work was supported by 21st century COE program, Nano Factory.@footnote 2@Y.H. Wu, et al., Adv. Mater., 14 (2002) 64. @footnote 3@M. Hiramatsu, et al., Rev. Sci. Instrum., 67 (1996) 2360.

PS-TuP12 Surface and Gas-phase Reactions in Plasma CVD using Cu(EDMDD)@sub 2@ as Source Material*, K. Takenaka, M. Takeshita, M. Kita, K. Koga, M. Shiratani, Y. Watanabe,* Kyushu University, Japan*; T. Shingen,* Asahi Denka Kogyo K.K., Japan

We have demonstrated 1) deposition of Cu films which have a low resistivity of 1.85 µ@ohm@cm and a strong adhesion strength above 10 MPa to the TiN layer, and 2) conformal deposition of smooth Cu films of 20 nm in thickness in trenches 0.5 µm wide and 2.73 µm deep using H-assisted plasma CVD (HAPCVD), which has an advantage of controlling independently concentrations of Cu-containing radicals and H atoms.@footnote 1@ To obtain information on surface and gas-phase reactions in HAPCVD, we have studied electron impact dissociation processes of Cu(EDMDD)@sub 2@ as well as nucleation and island growth of Cu, which are closely related with smoothness of Cu films and their adhesion strength to their under-layer. Quadrupole mass spectroscopic measurements show that Cu(EDMDD)@super +@ is the dominant ionic product from Cu(EDMDD)@sub 2@ due to an electron impact at electron energy of 70 eV. Based on this result together with the ion-core model, Cu(EDMDD) is suggested to be the main neutral radical from Cu(EDMDD)@sub 2@ due to electron impact dissociation. In-situ FT-IR measurements also show that supply of H atoms to the surface of deposition film is quite effective in reducing its impurity concentration. Nucleation density has little dependence on the kind of materials of under-layer such as TiN, TaN, WN, and Si. The nucleation rate increases from 2.3x10@super 14@ m@super -2@s@super -1@ at the substrate temperature T@sub s@ = 120°C to 4.1x10@super 14@ m@super -2@s@super -1@ at T@sub s@ = 220°C with increasing T@sub s@, while a maximum nucleation density of 3x10@super 16@ m@super -2@ is obtained at T@sub s@ = 150°C. The maximum density is more than two orders of magnitude higher than that for thermal CVD, and the high density is considered to contribute to smoothness and high adhesion strength of Cu films. @FootnoteText@ @footnote 1@ K. Takenaka, et al., Proc. of ISTC 2002 (in press).

PS-TuP13 Sub-Millimeter Absorption Measurements of Temperature and Density in Fluorocarbon Plasmas*, **E.C. Benck**, K. Siegrist, D. Pusquellic,* 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. Initial measurements are being conducted with a backward-wave-oscillator (BWO) source and a liquid-He-cooled bolometer detector. The narrow linewidth (< 10 kHz) of the BWO is ideally suited for measuring the translational temperatures of radicals through the Doppler broadening of the absorption lineshape. Previous temperature measurements in an inductively coupled Gaseous Electronics Conference (GEC) Reference Reactor found all the radicals to have a translational temperature close to room temperature. Other spatially resolved plasma diagnostics, such as laser-induced fluorescence, in similar inductive sources found significantly higher rotational temperatures within the plasma. The disagreement between the diagnostic methods is being investigated by measuring the radial density and temperature distributions. Initial results indicate that the low temperatures being measured with the BWO are probably due to the geometry of the GEC Reference cell which has a large volume of gas surrounding the plasma. Therefore the line-integrated absorption signal of the BWO is being dominated by the cooler, denser gas surrounding the plasma.

PS-TuP14 Plasma Frequency Measurements for Absolute Plasma Density by Means of Wave Cutoff Method*, **J.H. Kim**,* Korea Research Institute of Standards and Science, Korea*; Y.H. Shin, K.H. Chung,* Korea Research Institute of Standards and Science

A plasma oscillation method@footnote 1@ and a plasma absorption method@footnote 2,3@ have been used for measurements of absolute electron density in a plasma. In this report, a newly designed method for precise measurements of absolute electron density in the plasma using plasma frequency is described. A microwave perturbation of a frequency is introduced to plasma from a network analyzer and transmits in the plasma. The transmitted wave at a distance from a radiating antenna is monitored using spectrum analyzer as scanning the perturbing frequency. The transmitted wave rapidly decays by wave cutoff at the plasma frequency, which gives the absolute electron density. The propagating waves of some frequency including plasma frequency are characterized. The measured plasma frequency by this method is coincident with that obtained by the plasma oscillation method. The measured plasma densities are also compared with those got by using a double Langmuir probe over wide parameter range (gas composition, input power and gas pressure). @FootnoteText@ @footnote 1@T. Shirakawa and H. Sugai, Jpn. J. Appl. Phys. Vol. 32, 5129 (1993). @footnote 2@H. Kokura et al., J. Appl. Phys. Vol. 38, 5262 (1999). @footnote 3@K. Nakamura et al., J. Vac. Sci. Technol.A 21, 325 (2003).

Plasma Science and Technology
Room 314 - Session PS1-WeM

Plasma Processing of Nanostructures and Nanomaterials

Moderator: S. Samukawa, Tohoku University, Japan

8:20am **PS1-WeM1 The Study of Plasma Etching Limits Using Nanometer-Scale Self-Assembled Arrays*, Y. Zhang*,** *T.J. Dalton,* IBM

Fine patterning of semiconductor nano-scale features at the sub-20nm region is a challenging task. Among the nanometer scale features of importance in microelectronics and bio-microelectronics applications are: (1) open standing nano-features, i.e., a Si gate, and (2) small nano holes, i.e., an array of vias with nanometer scale diameter. The rapid shrinking of conventional CMOS technology is quickly approaching a perceived scalability limit or "brick wall". Plasma etching of true nanometer scale features may also face its limits. For open standing nano-features, the main challenge (or soft limits) is CD control, e.g., line edge roughness (LER) control of sub-10nm Si gate lines. A LER tolerance of 10% for 10nm gates means controlling 1nm, which has about 1 layer of silicon atoms on each side of gates. For true nanometer scale via arrays, the diameter of the vias for sub-10nm sizes is approaching the sizes of reactive products, e.g., SiBr4, SiF4, and SiCl4. In this case, plasma etching may hit its ultimate limits ("hard" limits). In this study, self-assembled nanometer scale diblock copolymer arrays were used to generate large scale (across 200 mm wafers) sub-20 nanometer test structures. The nanometer hole arrays were used to tested plasma etching characteristics of different materials, i.e., silicon, silicon dioxide, and silicon nitride with different plasma chemistries, from fluorine, chlorine, to bromine to vary the sizes of reactive species, F, Cl, to Br, and etching byproducts, such as SiF4, SiCl4, to SiBr4, with the aim of finding the plasma etching limits. In this paper, we present our recent work on the challenges of pattering nano-features, e.g., decreasing patterning layer thickness, aspect ratio dependent etch (ARDE), selectivity, and limits for sub-10 nm scale holes. Underlying principle of the different etching chemistry and processing parameters and their advantage and drawback to etch nanometer scale features will be also discussed.

8:40am **PS1-WeM2 Insights into Nanoparticle Formation Processes in a Thermal Plasma Process*, C.R. Perrey*,** *C.B. Carter, T. Renault, A. Gidwani, R. Mukherjee, X. Wang, J. Hafiz, W.M. Mook, W.W. Gerberich, P.H. McMurry, J.V.R. Heberlein, S. Girshick,* University of Minnesota

As nanoscale metal and ceramic particles are increasingly considered for industrial applications, a fundamental understanding of the effects of processing on particle morphology is required. The size, shape, structure, chemistry, and resulting properties of nanoparticles are all potentially functions of the formation method. This study examines the structure and chemistry of both nanoparticle films and individual nanoparticles produced by hypersonic particle plasma deposition. The process utilizes a thermal plasma to generate nanoparticles which are then rapidly assembled to form nanostructured films; the mechanical properties of both the particles and the films appear to differ significantly from the bulk material of the same composition. Observations made by electron microscopy are used to analyze the materials at each stage of the process. The presence of nanoparticles with atomically flat planar defects and a spherical shape imply a rapid condensation and crystallization from the gas phase. This paper will illustrate studies involving the production of Si, SiC, and Ti nanoparticles and nanostructured films, allowing comparisons for the different materials.

9:00am **PS1-WeM3 Reactive Gas Condensation of Aluminum Nitride Nanoparticles*, C. Baker*,** *A. Ceylan, S.I. Shah,* University of Delaware

AlN nanoparticles were synthesized using Reactive Gas Condensation (RGC) technique in which a gas mixture of NH3 and N2 was used for the nitridation of aluminum vapors that were obtained by resistive evaporation of Al wire. NH3 served as the reactive gas while N2 served as both a carrier gas and a source for particle condensation. The process was carried out at a pressure range of 50 - 100 Torr in order to facilitate the condensation. X-ray diffraction (XRD) and X-ray photoelectron (XPS) analysis revealed that the samples deposited with more than 10% NH3 in N2 were composed entirely of hexagonal AlN nanoparticles. The particles were single crystal, as determined by electron diffraction in transmission electron microscopy. The particle size was controlled by varying the pressure of the gas mixture for high relative concentrations of NH3. AlN nanoparticles were dispersed in various liquids to enhance the fluid thermal conductivity. Results will be presented to show that the thermal conductivity of the liquid was considerably increased with the addition of minimal amount of AlN nanoparticles.

9:20am **PS1-WeM4 Properties of Carbon-based Nanofibers Grown by Low-pressure Plasma Enhanced Chemical Vapor Deposition*, J.B.O. Caughman*,** *L. Zhang, D.W. Austin, M.A. Guillorn, A.V. Melechko, V.I. Merkulov,* Oak Ridge National Laboratory

The role of the plasma in the growth of carbon-based nanofibers is being determined by related plasma conditions to the physical and electrical properties of the nanofibers. Forests of nanofibers, as well as single isolated nanofibers have been grown using an inductively coupled plasma source operated from 50 to 200 mTorr. The plasma is composed of hydrogen and either acetylene or methane as the carbon source, with the addition of diborane and/or nitrogen to modify the composition of the nanofibers. The plasma conditions are determined by using mass spectroscopy and optical emission spectroscopy. The electrical properties of the nanofibers are found by using a four-point probe method, where electrodes are deposited on individual nanofibers. Processing results show that acetylene utilization increases with input power and reaches values of 70 to 80 percent as the discharge transitions to the inductively coupled regime, which results in well-formed cylindrical nanofibers. Excessive carbon in the plasma results in an increase in amorphous carbon deposition on the nanofiber sidewalls. Substrate bias plays an important role in controlling the physical etching component during deposition, where a transition is made from an amorphous thin film to a cylindrical nanofiber to a damaged structure as the bias increases. The electrical characteristics of the nanofibers grown with the low pressure method are compared to those grown with a conventional DC plasma-based method, where the resistivity has been found to be nearly the same as polycrystalline graphite. Details of the effect of plasma properties and the effect of nitrogen and boron addition on the electrical/physical properties of the nanofibers will be presented.

9:40am **PS1-WeM5 Growth of Vertically Aligned Carbon Nanotubes Using a High Density Plasma CVD Process*, H.W. Wei,*** National Tsing Hua University, ROC*; K.C. Leou,* National Tsing Hua University, ROC, R.O.C*; M.T. Wei, K.J. Shen, C.H. Tsai, C. Lin,* National Tsing Hua University, ROC

Vertically aligned multiwall carbon nanotubes are grown on silicon substrates with Ni catalyst patterns using an inductively-coupled high density plasma chemical vapor deposition reactor. The plasma is produced by 13.56 MHz RF power and a feed gas of C@sub 2@H@sub 2@ and H@sub 2@ mixture at a pressure below 100 mtorr. A heated and DC biased subtrate stage is employed to allow low temperature and aligned growth of CNTs. Due to low pressure operation, the growth rate of the CNTs is relative low (50-200 nm/min.) while the diameter of the tubes ranges from 30 nm to 120 nm depending on growth conditions. Another feature of the patterned and aligned growth of the CNTs using this HDP-CVD process is that the density of CNTs is relatively low (10@super 8@ to 10@super 9@ 1/cm@super 2@) although the CNTs are directly grown on 5 µm x 5 µm catalyst patterns. This will result in a reduction of the shielding effect of electric field for field emission appication of the CNTs. Results from parametric study of CNTs properties based on Raman spectroscopy, TEM and field emission measurements with process conditions as well as measurements from a mass spectrometer and plasma emission actinometry (for H atom) will be presented. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

10:00am **PS1-WeM6 Correlation between Size of Clusters and Qualities of a-Si:H Films for SiH@sub 4@ High Frequency Discharges*, K. Koga*,** *N. Kaguchi, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Previously, we have shown that a reduction of amount of particles below 10 nm in size (clusters) formed in SiH@sub 4@ high frequency discharges is the key to deposit hydrogenated amorphous silicon (a-Si:H) films of extremely small microstructure parameter R@alpha@ < 0.01. In this work, we have studied correlation between cluster size and a-Si:H film qualities by using the cluster suppressed plasma CVD method@footnote 1@ together with newly developed downstream cluster collection (DCC) method. The following results have been obtained in our experiment: 1) the DCC method offers a quite high sensitivity deduction of size and density of clusters above 1 nm in size and 10@super 4@ cm@super -3@ in the reactor; 2) An initial fill factor (FF@sub i@) of a n@super +@Si/a-Si:H/Ni Schottky solar cell gradually increases from 0.46 for mean cluster size d@sub c@= 9.0 nm to 0.48 for d@sub c@= 3.7 nm and significantly increases to 0.53 for d@sub c@= 1.6 nm. 3) The FF@sub i@ value increases with decreasing volume fraction of clusters. Experiments for studing correlation between amount of clusters of sub nm in size and film qualities

is underway. @FootnoteText@ @footnote 1@M. Shiratani, K. Koga, M. Kai, and Y. Watanabe, Thin Solid Films 427, 1(2003).

10:20am **PS1-WeM7 Study of Plasma-Nanoporous Silica Surface Interactions in Fluorocarbon and O@sub2@ Discharges: Comparison with SiO@sub 2@ and Organosilicate Glass***, X. Hua,* *G.S. Oehrlein, R.M. Briber,* University of Maryland, College Park*; P. Lazzeri, N. Coghe, M. Anderle,* Center for Scientific and Technological Research, Italy

We have investigated plasma surface interactions of nanoporous silica (NPS) films with porosities of up to 50%, SiO@sub 2@ and organosilicate films in either C@sub 4@F@sub 8@/Ar discharges (used for plasma etching) or O@sub 2@ plasmas (used for resist mask removal). Surfaces of the various materials after the above plasma processes were studied by x-ray photoemission spectroscopy as a function of process conditions. In addition, time-of-flight secondary ion mass spectrometry (in static or dynamic mode) was used to obtain additional information on the compounds formed on the surfaces of these materials, or on variations of elemental densities as a function of depth. The plasma-surface interactions of NPS are strongly modified relative to conventional SiO@sub 2@ or OSG. Several depth scales of these alterations exist: The surface and near-surface region (down to ~10 nm), intermediate depth (~50 nm), and the complete NPS film thickness to the interface with the substrate. In the surface/near-surface region the porosity of the NPS material increases the plasma-surface interaction area, which during fluorocarbon etching leads to differences in surface fluorocarbon film coverage for NPS relative to SiO@sub 2@ and associated changes in etching behavior. The larger depth scales are especially relevant for O@sub 2@ cleaning which strongly decreases the residual carbon content of both OSG and NPS down to intermediate depths and for NPS materials of 30% and 50% porosity produces deep penetration of fluorine down to the substrate-interface.

10:40am **PS1-WeM8 High Flux and Low Energy Neutral Beam Formation Using a Low Angle Forward Reflected Neutral Beam System***, D.H. Lee, S.J. Jung,* Sungkyunkwan University, South Korea*; K.H. Baek,* Samsung Electronics, South Korea*; C.J. Kang,* Samsung Electronics, South Korea, Korea*; G.Y. Yeom,* Sungkyunkwan University, South 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 particle such as positive ion and photons generated in the plasma. Charge-induced damage during the plasma etching is one of the serious problems that have to be solved for the deep 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. Among the techniques fabricating a neutral beam, 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 has been investigated in this study. Previous studies showed that, by the reflection of the ion beam at 5 degree angle of incidence, most all of the ions could be neutralized and nearly vertical SiO2 etching could be obtained for various fluorine based gases. In this study, for the formation of high flux and low energy neutral beam, a modified neutral beam source was proposed, and Si and SiO2 etch properties such as etch rate, etch selectivity, and etch profiles with fluorine-based gases using this system have been investigated. Also, the surface damage of the etched Si surface was investigated using TEM.

Plasma Science and Technology
Room 315 - Session PS2-WeM
Etching Difficult Materials

Moderator: C.B. Labelle, Advanced Micro Devices

8:20am **PS2-WeM1 Ion-enhanced Etching of High-k Dielectric Films with Mass-analyzed Ion Beam Irradiation***, K. Karahashi, N. Yamagishi,* MIRAI-ASET, Japan*; T. Horikawa,* MIRAI-ASRC/AIST, Japan*; A. Toriumi,* MIRAI-ASRC/AIST and University of Tokyo, Japan

As advanced high-k gate dielectrics are being developed to replace SiO@sub2@ in future generations of microelectronics devices, understanding their etch characteristics becomes vital for introducing the materials into the manufacturing process. We report on the interactions of high-k dielectrics, such as HfO@sub2@, Al@sub2@O@sub3@, with ionic species contained in plasma etching environments. To clarify the ion induced reactions in the fluorocarbon plasma, we employed the mass-analyzed ion beam apparatus that can irradiate a single ionic species to sample surfaces under an ultra-high vacuum condition. CF@sub3@@super+@, ion is found to chemically etch HfO@sub2@ and Al@sub2@O@sub3@ films, and the etch yield scaled linearly with the square root of ion energy with a threshold energy between 20 - 40 eV. This indicates that the etching reaction is limited by the momentum transfer to the etched film. Etching yields decreased monotonically with decreasing fluorine atoms contained in incident fluorocarbon ions (CF@subX@@super+@, X=1-3). In the case of CF@super+@, ion irradiation, the etching stopped after slightly etching HfO@sub2@ films. Then an amorphous fluorinated carbon (a-C:F) film was continuously deposited on the HfO@sub2@ surface. Using x-ray photoelectron spectroscopy analysis, it was confirmed that carbon accumulates on the surface at the early stage as CF@super+@ ion dose increases, so that the transition to the a-C:F deposition is caused by surface modification with CF@super+@ ion irradiation. This work was supported by NEDO.

8:40am **PS2-WeM2 Etching Characteristics of High-k Dielectric HfO@sub 2@ Films in Inductively Coupled Fluorine-Containing Plasmas***, K. Takahashi, K. Ono, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. Regarding gate dielectrics, the technological challenge continues for growing ultrathin SiO@sub 2@ films of high quality; however, the ultimate solution relies on high dielectric constant (k) materials. In integrating high-k materials into device fabrication, an understanding of the etching characteristics of the materials is required for their removal and for contact etching. This paper presents the etch rates and possible etch mechanisms for HfO@sub 2@ thin films on Si substrate in inductively coupled plasmas containing mixtures of CF@sub 4@/Ar, C@sub 4@F@sub 8@/Ar, or SF@sub 6@/Ar, as a function of gas composition, rf bias power, and surface temperature. The discharge was established at a gas pressure of 20 mTorr and an rf source power of 300 W. As the concentration of F-containing gases was decreased, the etch rate of Si decreased owing to the decreased amount of F radicals, while the etch rate of HfO@sub 2@ remained almost unchanged, resulting in an increase in etch selectivity of HfO@sub 2@ over Si. Increasing the bias power increased the etch rates of both Si and HfO@sub 2@; however, the increase in etch rate was more significant for HfO@sub 2@ than for Si, also resulting in an increase in selectivity. These results imply that the etching of HfO@sub 2@ relies primarily on the sputtering by ion bombardment, and the etch rates were typically on the order of 20 nm/min with a selectivity > 1 at large Ar concentrations and high bias powers. A comparison is made with the results of plasma and surface diagnostics, to gain a better understanding of the physics and chemistry underlying the processing, and to achieve higher selectivities. @FootnoteText@ This work was supported by NEDO/MIRAI Project.

9:00am **PS2-WeM3 Plasma Etching of High Dielectric Constant Materials on Silicon***, L. Sha, D.L. Ramirez, J.P. Chang,* University of California, Los Angeles

Novel plasma etching chemistries are needed to pattern high dielectric constant materials, such as ZrO@sub 2@ and HfO@sub 2@, to enable their integration in sub-100 nm complementary metal oxide semiconductor (CMOS) devices. In the paper we discuss the study of the reaction kinetics of etching ZrO@sub 2@ and HfO@sub 2@ in chlorine and boron trichloride chemistry in an Electron Cyclotron Resonance (ECR) high-density plasma reactor. The BCl@sub 3@/Cl@sub 2@ plasma was characterized by Langmuir probe, optical emission spectroscopy (OES), and quadrupole mass spectroscopy (QMS). The etch rate of ZrO@sub 2@ and HfO@sub 2@ were determined to scale linearly with the square root of ion energy in Cl@sub 2@ plasma, indicating that the etching reactions are limited by the momentum transfer to the etched film. The etching products in Cl@sub 2@ plasma were determined to be highly chlorinated metal chlorides and chlorine oxides. The relative abundances of metal tetrachlorides were increased at higher ion energy due to the enhanced surface chlorination. Addition of BCl@sub 3@ reduced the ion densities, but significant enhanced the metal oxides etch rate, due to the enhanced removal of oxygen. Silicon etch rate was suppressed with formation of the passivation layer of B-Si, resulting in the improved metal oxide etching selectivity with respect to silicon. The etching threshold energy for ZrO@sub 2@ and Si in BCl@sub 3@ were determined to be 21 eV and 28 eV, respectively, providing a range of operating conditions with very high etching selectivity. Increasing the electron temperature and ion density in BCl@sub 3@ plasma could further increase the etching selectivity. Under the same operating conditions, the HfO@sub 2@ etch rate is lower than ZrO@sub 2@ etch rate, due to the stronger Hf-O bonds.

9:20am **PS2-WeM4 Investigation of Etching Properties of Hafnium Oxide Based High-K Materials Using Inductively Coupled Plasma***, J. Chen,* National University of Singapore*; W.J. Yoo,* National University of Singapore, Singapore*; S.H.D. Chan,* National University of Singapore

The HfO-based high dielectric constant (K) materials are being investigated as the most promising candidates to replace the conventional SiO-based dielectrics for CMOS device applications. Development of etching processes for these materials is challenging since their etch products are mostly non-volatile and therefore adversely affect device properties due to difficulties to control effective gate length and to reduce contact resistance and Si over-consumption. In this work, we investigated etching properties of HfO@sub 2@, HfO@sub x@N@sub y@, HfSi@sub x@O@sub y@, HfAl@sub x@O@sub y@ deposited by CVD and PVD, using ICP of Cl@sub 2@/HBr/CF@sub 4@/O@sub 2@. The results showed that the etch rates of the HfO-based high-K materials were only ~ 100Å/min in CF@sub 4@ plasmas but increased up to 1000Å/min in Cl@sub 2@/HBr plasmas. The etch rates increased rapidly with increasing inductive power, rf bias power, and/or the amount of Cl@sub 2@. It was interesting to find out that in Cl@sub 2@ plasmas, etch rates varied differently depending on the chemical components added to HfO. That is, etch rates increased with the addition of Si or N, but decreased with the addition of Al. The XPS analysis showed that, a significant amount of fluorides (F: 10%~16%) existed on surfaces of all the HfO-based materials after CF@sub 4@ plasma etching, whereas amounts of chloride and bromide were little (Cl: 1.0%~2.2% and Br: 0.6%~1.7%) after Cl@sub 2@/HBr plasma etching. We suggest that non-volatile etch products from the CF4 plasmas are responsible for the low etch rates, whereas more volatile etch products from Cl@sub 2@/HBr plasmas result in higher etch rates. Analyzing the etch rates and XPS results for various concentrations of O in the HfO-based materials, we also found that low-reactivity of the Hf-O bonds and low-volatility of etch by-products from HfO-based materials could be responsible for the low etch rates.

9:40am **PS2-WeM5 Selective Dry Etching of SrBi@sub 2@Ta@sub 2@O@sub 9@/CeO@sub 2@ in the High Density Inductively Coupled Plasma Reactive Ion Etching***, S.I. Shim,* Korea University*; Y.S. Kwon, S.I. Kim,* Korea Institute of Science and Technology*; Y.T. Kim,* Korea Institute of Science and Technology, Korea*; J.H. Park,* Korea University

The dry etching and etch stop of the ferroelectric film on the silicon surface without damage is the key process of the self-aligned gate structure for the fabrication of Single Transistor Type Ferroelectric Memory. The high vertical etching angle is also necessary for the high integration. In this paper, etching characteristics and selective dry etchings of SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) film and CeO@sub 2@ film which is used for the buffer layer to improve the interface between SBT and silicon surface by using the Inductively Coupled Plasma Reactive Ion Etching (ICP-RIE) system with various Ar/Cl@sub 2@ gas mixtures were reported. The highest etching selectivity of SBT/CeO@sub 2@ was 6.8 and the vertical angle of SBT was 82°. The samples for etch were prepared by depositing CeO2 films with the thickness of 200 Å on Silicon substrates using rf sputtering of a Ce target in the reactive oxygen ambient. The SBT films with the thickness of 3000 Å were prepared on the CeO@sub 2@ film and Si substrate by MOD method. The capacitor-voltage (C-V) measurement shows there was no degradation of the ferroelectric characteristics after dry etching process. The SEM images and XPS data proved the etch stop was achieved successfully. For further investigation, N+/P diode junction and the metal ferroelectric insulator semiconductor filed effect transistor (MFISFET) with Pt/SBT/CeO@sub 2@/Si gate structure were fabricated. The I-V characteristics of the N+/p junctions and the drain current-drain voltage (I@sub D@-V@sub D@) and drain current-gate voltage (I@sub D@-V@sub G@) characteristics of the fabricated MFISFET show the etch stop process by using ICP-RIE system was successfully achieved without damage of silicon surface and degradation of ferroelectric characteristics.

10:00am **PS2-WeM6 High Rate Etching of SiC in Ultrahigh Density Plasmas Excited by Electron Cyclotron Resonance***, K. Nakamura, M. Tuda, M. Taki, K. Shintani, H. Sumitani,* Mitsubishi Electric Corporation, Japan

Silicone carbide (SiC) is a promising substrate material for advanced high power devices, high frequency devices, and microelectoromechanical systems, because of good electrical, mechanical, and chemical properties. Fabrication for these devices, deep etching of SiC with a high rate and high selectivity to mask material is required. Etching of SiC is known to be difficult since its bonding energy is relatively larger than those for conventional Si and GaAs. Recently, fast SiC etching with an etch rate of ~1 µm/min has been reported,@footnote 1,2@ where high density ICP and Helicon Plasma sources were used. However, a much higher etch rate is needed for the bulk micromachining (typically, etched depth >100 µm) of SiC substrates. In this study, we have developed fast SiC etching processes using a ultrahigh density plasma source excited by electron cyclotron resonance (ECR); the plasma density measured for Ar was 10@super 12@-10@super 13@ cm@super -3@, and the ion current density onto a substrate stage was more than 100 mA/cm@super 2@. Etching of 4H-SiC was performed in SF@sub 6@/O@sub 2@ plasmas by varying gas pressure, flow rate, O@sub 2@ concentration, microwave power, and rf-bias power. With increasing microwave and rf-bias powers, the SiC etch rate increased up to ~8 µm/min. A high etch rate (>5 µm/min) and selectivity (>50 to Ni) was simultaneously obtained under optimized conditions. These results show that ultrahigh density ECR plasmas are desirable for SiC bulk micromachining. @FootnoteText@ @footnote 1@ F. A. Khan and I. Adesida, Appl. Phys. Lett. vol.75 2268 (1999)@footnote 2@ P. Chabert, N. Proust, J. Perrin, and R. W. Boswell, Appl. Phys. Lett. vol.76 2310(2000) .

10:20am **PS2-WeM7 Chemical Mechanisms of Metal Etching in High Density Plasmas***, A.S. Orland, R. Blumenthal,* 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 based upon CO@sub 2@/NH@sub 3@ etching and a new etch chemistry based on CO@sub 2@/H@sub 2@ 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. Finally, the mechanism of etching will be compared with the mechanisms of CO/NH@sub 3@ and CO/H@sub 2@ etching which have been previously shown to etch by the formation of volatile metal formates and metal acetates through a plasma-surface reaction. All of these etching chemistries are plagued by carbide deposition at high concentrations of CO@sub 2@ or CO, and an explanation of the deposition mechanism will be given as well.

10:40am **PS2-WeM8 Low Energy Electron Enhanced Etching (LE4) of HgCdTe and III-V Semiconductor Materials***, J. Kim, T.S. Koga, C. Miclaus, H.P. Gillis, M.S. Goorsky,* University of California, Los Angeles*; G.A. Garwood, D.R. Rhiger, S.M. Johnson,* Raytheon Infrared Operations

The high energy ion bombardment involved in the reactive ion etching (RIE) process creates damage sites in the HgCdTe material which cause type conversion, among other problems. The ion energy can be reduced by using electron cyclotron resonance (ECR) plasma etching; however, the etched surfaces are not reliably stoichiometric or smooth. We have been exploring a new dry etching technique called low energy electron enhanced etching (LE4) to achieve low-damage, smooth, stoichiometric etched surfaces with high-resolution pattern transfer.@footnote 1@ In the LE4 process, electrons at energies 1-15 eV and reactive species at thermal velocities arrive at the surface. The LE4 technique, because it completely eliminates ion bombardment and relies on low energy electrons to control the etching chemistry, holds promise for eliminating the damage while retaining the beneficial features of RIE. LE4 experiments were performed on non-patterned, or photoresist (PR) mesa patterned Hg1-xCdxTe (x~0.3) epitaxial layers grown by molecular beam epitaxy (MBE) on (211)-oriented Cd1-yZnyTe substrate or (211)-oriented CdTe/Si substrate. In LE4 of HgCdTe, the sample was placed between the cathode and anode in a dc plasma. Dc bias was applied to the backside of the sample to control the electron current density to the surface. A mixture of Ar-CH4-H2-N2 (AMHN) was used as the etching gas. We will summarize results from mechanistic study to optimize etch condition, and demonstrate how electron energy, CH4 concentration, and sample temperature influence the etch rate, surface stoichiometry, and surface roughness. In addition, we will show some results of our AMHN LE4 process for III-V semiconductor materials (GaAs and InP). @FootnoteText@ @footnote 1@ J. Kim, T.S. Koga, H.P. Gillis, M.S. Goorsky, G.A. Garwood, J.B. Varesi, D.R. Rhiger, and S.M. Johnson, Extended Abstracts the 2002 U.S. Workshop on Physics and Chemistry of II-VI Materials 173 (2002).

Plasma Science and Technology
Room Hall A-C - Session PS-WeP
Poster Session

PS-WeP1 Experiemental Study of Real-Time Feedback Control of Ion Energy and Ion flux in Poly-Si Etch Process Using High Density Cl@sub 2@ Plasmas*, **K.C. Leou,*** National Tsing Hua University, ROC, R.O.C*; C.H. Chang, C. Lin,* National Tsing Hua University, ROC

In this study, we have demonstrated experimentally the real-time closed-loop control of both ion density and ion energy in a chlorine inductively coupled plasma etcher. To measure positive ion density, the trace rare gases-optical emission spectroscopy (TRG-OES) is used to measure the chlorine positive ion density. An rf voltage probe is adopted to measure the RMS rf voltage on the electrostatic chuck which is linearly dependent on sheath voltage. One actuator is a 13.56 MHz rf generator to drive the inductive coil seated on a ceramic window. The second actuator is also a 13.56 MHz rf generator to power the electrostatic chuck. The closed-loop controller is designed to compensates process drift, process disturbance, and pilot wafer effect and to minimize steady state error of plasma parameters. This controller has been used to control the etch process of unpatterned polysilicon. The experimental results showed that the closed-loop control had a better repeatability of plasma parameters compared with open-loop control. The closed-loop control can eliminate the process disturbance resulting from reflected power. In addition, experimental results also demonstrated that closed-loop control has a better reproducibility in etch rate as compared with open-loop control. Experiment results on SiO@sub 2@ etch show that real-time feedback control of both ion energy and flux also enhance the process stability of etch selectivity (Poly-Si to Oxide) in addition to the etch rate of poly-Si. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

PS-WeP3 Study of the Passivation Mechanisms Involved in the Silicon Deep Etching Cryogenic Process*, **X. Mellhaoui**, R. Dussart, A. Basillais, T. Tillocher, P. Lefaucheux, P. Ranson,* GREMI, France

Silicon etching is perfomed by cryogenic SF@sub6@/O@sub2@ plasma process. This process allows to obtain a high aspect ratio (depth/width > 10) and a high anisotropy. The plasma is created in an Inductively Coupled Plasma reactor. The silicon wafer is clamped on a chuck cooled with liquid nitrogen and controlled in temperature. A study of passivation mechanisms is necessary to perfectly control this process and to optimize the trench profiles. The passivating layer is a mixture of Si, F, O and S (SiO@sub x@F@suby@S@subz@). Previous XPS experiments have shown that the passivation layer is removed during the increase of temperature, which proves that the passivation layer is not mainly composed of SiO@sub2@. When destroyed, the passivation layer can be rebuilt with SiF@sub4@ and O@sub2@. This particular experiment was made and has revealed that the presence of sulphur is not necessary to build an efficient passivation layer. Experiments to better understand the passivation layer reconstruction and composition will be presented at the conference. In overpassivating conditions (high O@sub2@ flow), black silicon phenomena appear in trench bottom. Roughness and black silicon pattern depend on several parameters (temperature, bias voltage, O@sub2@/SF@sub6@ ratio). A statistical study made on the black silicon pattern will be also presented.

PS-WeP4 Etching Characteristics in Novel Internal Linear Inductively Coupled Plasma Antenna for Flat Panel Display Applications*, G.Y. Yeom,* ***K.N. Kim****, Y.J. Lee,* Sung Kyun Kwan University, South Korea*; B.U. Cho, J.K. Lee,* Pohang University Science and Technology, Korea*; M.A. Lieberman,* University of California at Berkeley

The flat panel display (FPD) industry, especially for liquid crystal display (LCD) has been experiencing an impressive growth for the last 10 years, and moving to large generation sizes such a 1200mmX1500mm for reducing manufacturing costs, although third (550mmX650mm) and fourth generation (680mmX880mm) glass substrates are also available. Therefore, large-area plasma sources are needed to meet the plasma processing in display manufacturing plasma processing (PECVD, ETCH, and ASHING) and, to decrease the process time, high density plasma sources are required. In this study, large-area plasmas with inductive coupling of extended internal linear- antennas have been proposed promising candidate for the efficient high-density plasma source. The process chamber was designed as a rectangular mainly for FPD application and was made of stainless steel. The inner size of the chamber was 1020mmX830mm. To improve both the plasma density and the uniformity of internal ICP source, several internal-type linear antenna designs have been employed. In this presentation, the effects of various linear-antenna designs and process conditions on the plasma characteristics, such as plasma species and density, electron temperature, and plasma uniformity in this large area plasma source 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. The results showed a strong relationship between the combination of the antenna configuration and plasma characteristics such as density and uniformity. The etch uniformities of SiO@sub2@ etched using C@sub4@F@sub8@(NF@sub3@)/He/O@sub2@ gas mixtures showed the similar trend as that of Ar@super+@ ion density.

PS-WeP6 Inductively Coupled Plasmas in Cl@sub 2@/O@sub 2@ Mixtures: Modeling and Experiment*, **A.M. Efremov,*** Ivanovo State University of Chemistry and Technology, Russia*; C.I. Kim, D.P. Kim,* Chung-Ang University, Korea

Microwave thin films resonators have been integrated with complex perovskite materials Ba(Mg@sub 1/3@Ta@sub 2/3@)O@sub 3@ (BMT) and Ba(Zn@sub 1/3@Ta@sub 2/3@)O@sub 3@ (BZT), which are very perspective materials due to excellent microwave properties. However, plasma etching in Cl-base gases is obstructed by two main problems. First problem is low etching rate due to low-volatility of metal-chlorides, which can be cleaned by strong ion bombardment. But, it is undesirable to avoid defects in structure. Second problem is the deviationsof stoichiometry on the surface after the etching due to various partial etching yields. The origins of these problems are also caused by low and different volatilities of reaction products. Therefore improvement of BMT and BZT etching technology should follow by the way of improvement of efficiency of chemical mechanism through the increasing of etching products volatility. In this way, Cl@sub 2@/O@sub 2@ mixture is very promising environment. The reason is that the formation of high-volatile metal-oxy-chlorides (M-ClO) is expected. We investigated plasma characteristics, plasma mass content and kinetic dependencies of both neutral and charged particle formation and decay in Cl@sub 2@/O@sub 2@ gas mixture. For these purposes we used a combination of experimental methods (OES, Langmuir probe, QMS) and a plasma modeling on the base of self-consistent solution of Boltzmann kinetic equation together with balance kinetic equations for neutral and charged particles in a quasi-stationary approximation. It was found that the change of O@sub 2@/(Cl@sub 2@+O@sub 2@) mixing ratio from 0 to 100% leads to an increase of electron average energy and electron energy distribution function deformation. The main mechanisms of Cl and O atom formation are the direct electron impact dissociation of corresponding molecules while the contribution of all possible secondary processes is not significant in the case of a relatively low O@sub 2@ addition.

PS-WeP8 Atomic Layer Etching of Silicon using a Low Angle Forward Reflected Ar Neutral Beam*, **S.D. Park**, D.H. Lee,* Sungkyunkwan University, Korea*; G.Y. Yeom,* Sungkyunkwan University, Korea, South Korea

Atomic layer etching (ALE) is one of the important technologies for the fabrication of future nano-scale devices, because current dry etching techniques are not capable of etching with atomic layer resolution because of their high etch rates. In addition, relatively high energy of the ions can damage the crystal surface. Therefore, many studies on ALE of Si have been reported in recent years to develop a technique to etch materials layer-by-layer. But, these previous methods may show charging damage due to the charged particles such as positive ions and photons generated in the plasma. Therefore, in this study, ALE of Si was carried out using a sequential Cl@sub 2@ adsorption and an Ar neutral beam irradiation instead of ion beam. Low energy Ar neutral beam was generated by a low-angle forward reflected neutral beam technique. ALE of Si is a cyclic process consisting of 4 steps: (1) adsorption of Cl@sub 2@ on Si surface, (2) evacuation, (3) Ar neutral beam irradiation to the surface, (4) evacuation of etch products. The etch process parameters for optimizing the atomic layer etching of Si are Cl@sub 2@ gas exposure time, Ar neutral beam irradiation time, Ar neutral beam energy, etc. It is expected that the atomic layer etching of Si should be limited to 0.68 nm per cycle, which corresponds to the half mono-layer thickness of Si. The resulting step height and surface damage was estimated using transmission electron microscopy (TEM). The step height divided by the total number of ALE cycles yielded the etch rate per cycle. A scanning electron microscope (SEM) was used to observe as-etched Si profiles and an atomic force microscope (AFM) was used to analyze the surface topography.

PS-WeP9 Molecular Beam Mass Spectrometry of the Microwave Discharge in Methane/Argon Gas Mixture*, M. Misina, **P. Pokorny**,* Institute of Physics ASCR, Czech Republic

Mass spectrometry (MS) of the neutrals in a processing plasma requires extraction of a gas sample through an orifice, ionization, mass separation and detection. Radicals are detected by the appearance potential MS (APMS).@footnote 1@ APMS relies on the difference in the electron energy threshold for ionization of a radical by a simple electron impact ionization and for production of an fragment ion from a molecule by dissociative ionization. However, the absolute measurement of the radical density is complicated by the interaction of the radicals with the walls during the transport from the extraction orifice to the ionization source. This is especially true for species with a high sticking coefficient. Therefore, the molecular beam MS (MBMS) was developed.@footnote 2@ MBMS includes more stages of differential pumping with several orifices by which a beam of neutrals from the plasma is extracted into the ionization chamber of a MS. In this paper the concentration of radicals and the composition of the neutral gas in the microwave electron-cyclotron-resonance methane/argon plasma for DLC film deposition was measured by APMS and MBMS for a range of process parameters such as microwave power, working gas composition and total pressure. The total pressure in the experiment ranged from 0.1 to 1 Pa. The microwave power up to 800 W was used. The most abundant radical was methyl with a concentration of in the range of the order of 10@super 12@ cm@super -3@. A high degree of dissociation and consumption of the methane in the ECR discharge was observed. In fact, the hydrogen dissociated from the methane was the dominant component of the working gas at higher microwave powers. @FootnoteText@@footnote 1@ P. Kae-Nune, J. Perrin, J. Guillon, J. Jolly, Plasma Sources Sci. Technol. 4 (1995) 250-259.@footnote 2@ H. Singh, J. W. Coburn, D. B. Graves, J. Vac. Sci. Technol. A 17(5) (1999) 2447-2455.

PS-WeP10 Spatio-temporal Characterization of Pulsed, Electron Beam Produced Plasmas*, **S.G. Walton**, D. Leonhardt, C. Muratore, D.D. Blackwell, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

In plasma-based materials modification, regulating the flux of ion, neutral, and radical species at the substrate surface is a critical component of process control. The plasma density determines the flux and the electron temperature influences the energy of these species and so both can be used to regulate reactive species at the substrate. Modulated plasma production as well as remote plasma sources are often employed to control the relative ion flux and energy through temporal or spatial variations in the bulk plasma. In this paper, spatio-temporal characterizations of pulsed, electron beam-generated plasmas will be presented. Mass and time-resolved measurements of ion fluxes and energy distributions are presented and correlated to measurements of the plasma density and electron temperature. Previous work has shown that energetic electron beams are efficient at producing high-density plasmas (n@sube@ > 10@super11@ cm@super-3@) with low electron temperatures (T@sube@ < 1.0 eV) over the volume of the beam. Outside the beam, ion-neutral and electron-ion interactions alter the ion densities and flux. Temporal variations in the density, electron temperature, and flux have been observed during all phases of pulsed plasma production. Measurements are presented for a range of operating pressures, pulse widths, duty factors, and electron beam-to-electrode distances for plasmas produced in argon, nitrogen, and oxygen. The results are used to identify methods by which the ion fluxes and energies can be controlled. This work supported by the Office of Naval Research. @FootnoteText@ Muratore, C., ASEE/NRL Postdoctoral Research Associate; Blackwell, D.D., SFA Inc., Largo, MD.

PS-WeP11 Experimental Characterization of a Pulsed Inductively Coupled Plasma*, **C.H. Chang**,* National Tsing Hua University, ROC*; K.C. Leou,* National Tsing Hua University, ROC, R.O.C*; S.J. Wu, M.L. Gong, T.L. Lin,* National Tsing Hua University, ROC

The basic properties of a pulsed low pressure inductively-coupled plasma has been characterized by using various diagnostic tools, including a RF impedance meter, a Langmuir probe, a 36 GHz interferometer and optical emission spectroscopy. These tools have been modified from conventional ones to measure time resolved properties of the discharge. In addition to plasma density, plasma potential and electron temperature, the Langmuir probe has also been used to extract the electron energy probability function (EEPF) of the plasma. Measurement results show that high energy (roughly E > 10 eV) electrons are lost quickly after the driving RF power is turned off. The low energy part of the electrons remains nearly unchanged during the entire off period. The electron temperature thus drops quickly while plasma density changes little during RF off period as observed in other studies. Spatial-temporal behaviors of plasma density have also been measured. The radial distribution of plasma density only change slightly at different times of the RF on or off periods although the overall plasma density varies significantly. The electric properties of the discharge was measured by a home made impedance meter which detects the time varying amplitude and phase of the RF voltage and current, and thus net input RF power and complex impedance of the discharge. For different waveforms of modulation, such as square, triangular, sinusoidal and trapezoidal, impedance meter measurements show that, when the RF power is turned on, there is always a transient surge of RF voltage and current on the inductive coil, thus the net input power into the plasma. The temporal profiles of electric properties, however, do not vary significanly for different types of modulations. Comparison of probe and impedance meter measurements to interferometer and OES measurements will also be presented. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

PS-WeP12 Effect of Gas Heating in a High Density Pulsed Plasma Discharge*, D.J. Economou, **S.K. Nam**,* University of Houston

Owing to their importance, power-modulated plasmas have been studied both experimentally and computationally. However, the effect of gas heating in pulsed discharges has not been studied in detail. In contrast, there are numerous studies of gas heating in continuous wave discharges. A two-dimensional self-consistent model and simulation tool were developed to study the spatio-temporal dynamics of a pulsed power (square-wave modulated) inductively coupled argon discharge, with emphasis on gas heating effects. The coupled equations for plasma power deposition, electron temperature, charged and neutral species densities, and gas temperature were solved to obtain the space-time evolution of the discharge in a Gaseous Electronics Conference (GEC) ICP reference cell. The effect of control parameters such as power, duty ratio, pressure, and pulse frequency on the evolution of discharge properties (electron density, electron temperature, gas temperature) was investigated. Simulation results on discharge properties were in good agreement with available experimental data. @FootnoteText@ Work supported by the National Science Foundation.

PS-WeP13 A Model of Feature Profile Evolution for Nanometer-Scale Control of Etched Profiles and Critical Dimensions*, K. Ono, **Y. Osano**, A. Sano, K. Takahashi, Y. Setsuhara,* Kyoto University, Japan

As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma etching technology. The precise control of etched profiles and critical dimensions (CDs) is still one of the most important issues to be addressed, particularly in gate etch processes. In developing the technology to meet these demands, the modeling or simulation is an attractive approach, which significantly contributes to optimize complex processes in the fabrication of microelectronic devices. This paper presents a model of the feature profile evolution for nanometer-scale control of the profile and CD during etching of poly-Si gate electrodes in high-density chlorine- and bromine-containing plasmas. The model employs a full matrix approach with the volume density function in the entire computational domain for the materials being etched. This approach enables us to take into account surface reaction processes of enormous complexity that would occur during etching, particularly multilayer adsorption or reaction kinetics on feature surfaces, which the usual string algorithm with Langmuir adsorption scheme is hard to deal with. The model includes the transport and surface reaction kinetics of ions and neutrals in microstructures, based on our present understanding: neutral adsorption, geometrical shadowing, surface reemission or reflection of ions and neutrals, localized charging of feature surfaces, purely chemical etching, physical sputtering, ion-assisted reactions, and surface inhibitor deposition. The numerical results indicated that a thin passivation layer of surface inhibitors on feature sidewalls, surface temperature, and charging of mask layers play a key role in achieving the nanometer-scale control in gate etch processes.

PS-WeP14 Selected Modifications of PE and PTFE Surfaces by Means of a Modified RF N@sub 2@ Plasma*, **N. Vandencasteele**, F. Reniers,* Universite Libre de Bruxelles, Belgium

Plasma techniques are often used to modify polymer surfaces. However, due to the great variety of the species created in a plasma (neutrals, ions, electrons), the resulting surface modification is often poorly controlled, and the mechanisms of surface reaction poorly understood. In order to try to better control and undersand these processes, we have modified the geometry of a RF plasma chamber in order to be able to filter the species

reaching the surface, allowing only the neutrals and the electrons to reach the surface, depending on the electrode bias. The selected effect of the nitrogen ions was the subject of another study.@footnote 1@ PE and PTFE surfaces have been exposed to this modified N@sub 2@ RF plasma. The plasma was characterized by optical emission spectrometry. A variation of the densities of the active species relative to the cathode position is evidenced. The samples were afterwards characterized by XPS, water contact angle measurements and AFM (for surface roughness). A strong correlation between the surface energy, the nitrogen concentration on the surface, the plasma characteristics (DC-bias and RF power) and the treatment time is shown. A deconvolution of the C1s and N1s peaks show a progressive functionalisation sequence of the surface. The effect of the polarity of the native bonds (C-H in PE and C-F in PTFE) on this sequence is studied. @FootnoteText@ @footnote 1@A. Wagner, D.H. Fairbrother, F. Reniers, Plasma and Polymers 8 (2003) 119-134.

PS-WeP15 Principle of a Beam Profile Controlled Linear Ion Beam Source and Application Examples*, **M. Nestler**, D. Roth,* Roth & Rau AG, Germany*; F Scholze, M. Tartz,* Institut f@um u@r Oberfl@um a@chenmodifizierung Leipzig e.V., Germany*; M. Zeuner,* Ion+Tech GmbH, Germany*; H. Neumann,* Institut f@um u@r Oberfl@um a@chenmodifizierung Leipzig e.V., Germany

We present a microwave excited ECR (electron cyclotron resonance) type low energy linear ion beam source with a special grid system for cleaning, surface treatment, etching, figuring, surface modification and thin film deposition. By means of a modular design with basic module length of 400 and 600 mm this source is easily scalable up to some meters for production environment. Fitting this source with a special designed, segmented multi-aperture three grid system and power supplies in combination with a variable electrical switcher, which allows a changing of the pulse length of the accelerator voltage applied on each segment, the profile of this low energy ion beam is adaptable on different process requirements. We discuss the measured beam profiles in correlation to the controlling principles by using inert and reactive gases and draw up the technological possibilities for this new broad beam ion source by means of selected examples. Its integration into an in-line production equipment is demonstrated.

PS-WeP16 Creation and Characteristics of Miniature Microwave Plasmas*, **J. Narendra**, T.A. Grotjohn, 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 3 mm. The discharge characteristics investigated include microwave power density, plasma density, electron temperature and gas temperature. The outcome of this investigation is an understanding and quantification of the microwave power density needed to operate small discharges of specific sizes, shapes, pressures, and gas compositions. The microwave plasma source technology used in this investigation is a microstripline based plasma source with the discharge created in a quartz tube of 0.3 mm to a few mm in inside diameter. A microstripline is used to couple 2.45 GHz microwave energy into a discharge confined in a tube orientated perpendicular to the stripline conductor. The discharge formed often is a surface wave discharge. The plasma compositions investigated include argon, nitrogen, air, and hydrogen discharges. The pressure range investigated ranged from 100 mTorr to 1 atmosphere. The diagnostic measurements were 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@super 3@ and the plasma densities are above 10@super 13@ cm@super -3@. A specific application to be discussed is the plasma-assisted deposition of coatings on the inside of tubes.

PS-WeP17 Laboratory Exercises for a Technician-Level Course in Plasma-Aided Manufacturing*, **D.M. Hata**,* Portland Community College

Portland Community College, through a grant from the National Science Foundation's Advanced Technological Education Program, has developed educational materials for a technician-level course in plasma-aided manufacturing and has prototyped a suite of supporting laboratory exercises. These educational materials were classroom tested during Winter Term of 2003 in PCC MT 240 RF Plasma Systems course. Thirty-three second-year students used the instructional materials and performed the laboratory exercises. Four faculty enhancement workshops are scheduled during the next year and a half to equip other community college faculty to teach a similar course at their institutions. This paper or poster session will provide an overview of the laboratory exercises developed to date.

Plasma Science and Technology
Room 314 - Session PS1-WeA

Mechanisms in Plasma-Surface Interactions

Moderator: E. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS1-WeA1 PECVD of Thin Films: The Study of the Plasma-surface Interaction by Means of In Situ Plasma and Film Diagnostics*, M.C.M. van de Sanden,*** Eindhoven University of Technology, The Netherlands **INVITED**

Plasma enhanced chemical vapor deposition (PECVD) is now a well established technique to obtain various high quality films for e.g. micro-electronic, photovoltaic, scratch resistant or abrasive applications. Although widely applied in industry, fundamental knowledge on the actual plasma deposition mechanism is to a large extent unknown. The reason is the complexity of the problem: to unravel the deposition mechanism requires a simultaneous investigation of the plasma phase, the plasma-surface interaction and the film properties using in situ plasma and film diagnostics. The need to understand the mechanism is evident since the development and design of new functional materials and up scaling of the technique to large areas involves detailed and generic knowledge of the plasma-surface interaction. In this talk I will discuss the approach our group has undertaken to investigate the deposition mechanism of a limited number of model systems: the fast plasma deposition of hydrogenated amorphous silicon, carbon and silicone films utilizing a remotely expanding thermal plasma. I will discuss the measurement of radical and ion densities using sensitive plasma diagnostics such as cavity ring down spectroscopy and (modulated beam) appearance potential mass spectrometry. From measurements using the time-resolved version of these diagnostics, taken in the afterglow of a small perturbation of the plasma, plasma and surface reaction probabilities of selected radicals are determined. The results are compared with molecular dynamics simulations of the plasma-surface interaction and are discussed in relation to in situ characterizations of the chemical and structural composition of the film surface of the growing film.

2:40pm **PS1-WeA3 Plasma Nitriding and Reactive Deposition in Electron Beam Generated Plasmas****, C. Muratore**, *D. Leonhardt, S.G. Walton, D.D. Blackwell, R.F. Fernsler, R.A. Meger,* Naval Research Laboratory

A molecular gas based electron beam generated plasma provides a significantly higher atomic ion flux than molecular ion flux. Additionally, the well-defined geometry of the electron beam gives rise to a high spatial dependency of the plasma specie flux due to gas phase reactions between the beam edge and surface to be modified. To investigate the utility of the unique features associated with electron beam generated plasmas for materials processes, planar electron beams were used for plasma assisted nitriding and reactive sputter deposition. Stainless steel and other metals were exposed to electron beam generated plasmas containing mixtures of nitrogen and other gases at appropriate treatment temperatures to produce nitrided surface layers. The activation energy for nitriding was determined for stainless steel and other metals, and found to be lower than values associated with other plasma assisted nitriding processes. Thin films were reactively sputtered at equivalent total ion fluxes with variations in only plasma chemistry (e.g., N@super +@/N@sub 2@@super +@ flux ratios). All materials were characterized using standard techniques including atomic force microscopy, X-ray diffractrometry, electron microscopy and nanoindentation. Observed trends in microstructural features and materials properties correlate well to the measured plasma characteristics. @FootnoteText@ @footnote *@This work is supported by the Office of Naval Research. Muratore, C., NRL/ASEE Postdoctoral Research Fellow; Blackwell, D.D., SFA Inc., Largo, MD 20744.

3:00pm **PS1-WeA4 Angular Dependence of SiO@sub 2@, Si and Si@sub 3@N@sub 4@ Etch Yield in Fluorocarbon Gas Chemistries by using Plasma Beam*, K. Kurihara,*** *A. Egami, M. Nakamura,* ASET, Japan

A plasma-beam irradiation apparatus, which can control plasma parameters independently, such as ion energy, radical/ion composition and incident angle of ions, is very useful to examine the plasma-surface interactions under a real etching environment for constructing a process simulator without experiments of trial and error. We measured etch yield dependence on the incident angle of ions for Si, SiO@sub 2@, and Si@sub 3@N@sub 4@ substrates under the three conditions of Ar gas and two different fluorocarbon gas chemistries. One provides low selectivity of SiO@sub 2@ to Si using CF@sub 4@/Ar gas mixture (low selective mode), and the other provides high selectivity of that using CF@sub 4@/C@sub 4@F@sub 8@/Ar gas mixture (high selective mode). As for physical sputtering using Ar plasma, the etch yield at incident angle of 60 ° (oblique incidence) was about 4 times larger than that at incident angle of 0 ° (normal incidence) for all substrates at the ion energy of 530 eV, and this tendency was kept at the low ion energy of 120 eV. On the other hand for the case of CF@sub 4@/Ar gas chemistry, the etch yield of the oblique incidence was about 1.4 times larger than that of the normal incidence at the ion energy of 530 eV, but at that of 120 eV the etch yield did not increase with the increase in incident angle. In the case of etching reaction proceeded chemically by fluorocarbon gases, the angular dependence on the etch yield was influenced by the ion energy. The gas chemistry also affected the angular dependence on the etch yield. The etch yield of Si@sub 3@N@sub 4@ weakly depended on the incident angle in the case of the low selective mode, but that strongly depended on the incident angle in the case of the high selective mode. Concerning Si and SiO@sub 2@ substrates the angular dependence has no difference under above two modes. We will discuss the relation between composition of surface reaction layer and the etch yield. This work was funded by NEDO.

3:20pm **PS1-WeA5 Reduction Mechanism of VUV Radiation Damages in Pulse-Time-Modulated Plasma Processes*, Y. Ishikawa*,** *M. Okigawa,* Tohoku University, Japan*; S. Yamasaki,* National institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

In plasma processing using high-density plasma, vacuum-ultraviolet (VUV) radiation damage is one of the most serious problems. The electrical characteristics of dielectrics directly exposed to plasma are affected by plasma-emitted VUV radiation. VUV radiation with a higher photon energy than the SiO@sub 2@ band gap energy (8.8 eV) can generate electron-hole pairs in the irradiated dielectric films. The generation of electron-hole pair increases the charge densities trapped in the SiO@sub 2@ bulk and SiO@sub 2@/Si interface, affecting the conductivity of the SiO@sub 2@ layer. This results in dielectric breakdown, shorter lifetime of minority carriers, and a flat band voltage shift in transistors. Thus, reducing the VUV radiation damage is important for improving the reliability of semiconductor devices. To realize these requirements, we proposed a pulse-time-modulated plasma (pulsed plasma). In this paper, to understand the reduction mechanism of VUV radiation damages using pulsed plasma, we investigated the time dependence of defects (E' center) generation in the SiO@sub 2@ film by altering the pulse-on and off time. We found that the E' center was increased during the pulse-on-time and was also reduced during the pulse-off time. It is speculated that the generation and loss of E' center was progressed at the time constant of µmseconds. As a result, the pulsed plasma could drastically reduce the generation of E' center in the SiO@sub 2@ film and could eliminate VUV radiation damages in comparison with the continuous plasma.

3:40pm **PS1-WeA6 IRIS Investigations of Gas Phase Species in Fluorocarbon Plasmas*, I.T. Martin*,** *E.R. Fisher,* Colorado State University

Fluorocarbon (FC) plasmas are widely used for FC film deposition and the etching of Si-based materials. Investigating a specific molecule during plasma processing of a substrate can yield information on its role in the chemistry occuring at the plasma surface interface. CF@sub 2@ is a particularly interesting species in FC plasmas because its role differs in various plasma systems. CF@sub x@ and C@sub x@F@sub y@ radicals have been cited as FC film deposition precursors, while other work has shown cases where CF@sub 2@ is not a deposition precursor.@footnote 1,2,3@ We have used our imaging of radicals interacting with surfaces (IRIS) method to measure the surface interactions of CF@sub 2@ radicals with Si substrates during plasma processing. CF@sub 2@ surface loss coefficients determined for 25-200W C@sub 3@F@sub 8@ and C@sub 4@F@sub 8@ plasmas show relatively high levels of scattering, which indicates that CF@sub 2@ radicals are produced at the surface in these systems. One advantage of the IRIS system is our ability to collect data for multiple molecules in a single plasma system. Experimental excitation spectra have verified the presence of CF in our FC systems and have been used to determine the rotational temperatures (@theta@@sub R@) of CF in the plasmas. Trends in @theta@@sub R@ are discussed as a function of plasma input power and source gas. Surface reactivity studies will determine if CF contributes to CF@sub 2@ scatter in these systems. Preliminary investigations of SiF@sub 2@(g) formation at the surface will also be presented. @FootnoteText@ @footnote 1@ R. d'Agostino, et al., in Plasma Deposition, Treatment, and Etching of Fluorocarbons, edited by R. d'Agostino (Academic Press, Inc., San Diego, 1990) p.95-143.@footnote 2@ S. Samukawa, AIP Conference Proceedings 636, 95-107 (2002).@footnote 3@ K. Sasaki, et al., Thin Solid Films 374(2), 249-255 (2000).

4:00pm **PS1-WeA7 Fluorocarbon-based Plasma Etching: The Role of the Energy Distribution of Bombarding Ions**, *R. Silapunt, S. Williams,* ***A.E. Wendt,*** University of Wisconsin, Madison*; K.H.R. Kirmse, L. Losey,* Texas Instruments

In fluorocarbon-based plasma etching of dielectrics, an overlying thin fluorocarbon film, deposited on the substrate during etching, strongly affects etch rate and etch selectivity.@footnote 1@ Here we report on recent results that suggest that the energy distribution of bombarding ions (IED) has a significant effect on the thickness of this polymer layer, subsequently affecting etch rate and selectivity as well. Specifically, we have narrowed the IED while keeping other process conditions unchanged by tailoring the shape of the RF voltage waveform used for substrate bias. Significant improvements in etch selectivity for SiO@sub2@ over silicon, SiO@sub2@ over photoresist and organosilicate glass (OSG) over silicon nitride and silicon carbide have been obtained by using a narrow IED compared to the broad IED resulting from a sinusoidal bias waveform. X-ray photoelectron spectroscopy (XPS) has been used to determine the thickness of the overlying fluorocarbon film as a function of bias voltage for both narrow and broad IEDs. The results show a strong inverse correlation between film thickness and etch rate, suggesting that the sensitivity of this polymer film to the IED is the key to observed improvements in selectivity.@footnote 2@@FootnoteText@@footnote 1@ G. S. Oehrlein et al., JVST A 15, 1881 (1997)@footnote 2@ Supported by SRC (TI custom funding) .

4:20pm **PS1-WeA8 Investigating the Fundamental Mechanism of Surface Smoothening of Plasma-Deposited Amorphous Silicon Thin Films through Atomistic Simulations**, ***S. Sriraman,*** *S. Agarwal, E.S. Aydil,* University of California, Santa Barbara*; D. Maroudas,* University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. Nevertheless, the deposition mechanism of a-Si:H films and the fundamental surface processes that determine the surface morphology during deposition are still not well understood. Under conditions of low SiH@sub 4@ dissociation in the plasma, the dominant precursor for deposition is the SiH@sub 3@ radical. The remarkable smoothness of the a-Si:H films grown under these conditions has been used to conclude that the deposition precursor is very mobile and that it can fill surface valleys after adsorbing onto the film. Using molecular-dynamics (MD), molecular-statics, and Monte Carlo methods, we studied the growth of a-Si:H on initially H-terminated Si(001)-(2x1) surfaces; the films were grown through MD simulations of repeated impingement of SiH@sub 3@ precursor. The relationship between the structure, H coverage, morphology, and reactivity of plasma deposited a-Si:H film surfaces was investigated. Surfaces of a-Si:H films grown with SiH@sub 3@ as the sole deposition precursor were found to be remarkably smooth due to a valley-filling mechanism where mobile precursors, such as SiH@sub 3@ and Si@sub 2@H@sub 6@, diffuse and react with dangling bonds present in surface valleys. Surface transport of these adsorbed species may be driven by the surface Si-Si bond strain distribution, as well as the surface reactivity and morphology. Mobility of the surface species maybe mediated through the formation of over-coordination defects as weakly chemisorbed SiH@sub 3@ diffuse on the surface. Our analysis of the mechanism of SiH@sub 3@ precursor diffusion on the c-Si and a-Si:H surfaces will be presented. In particular, we emphasize the role of Si-Si bond strains in mediating the valley-filling mechanism leading to smooth film surfaces and the identity of the mobile precursor state.

4:40pm **PS1-WeA9 Study of SiO@sub 2@ Plasma Etching with Off-normal Mass-analyzed CF@sub x@@super +@ Ion Beam Irradiation**, ***K. Yanai,*** *K. Karahashi, K. Ishikawa, M. Nakamura,* Association of Super-Advanced Electronics Technologies, Japan

To clarify the elementary surface reactions in the fluorocarbon plasma etching, the mass-analyzed CF@sub x@@super +@ (x = 1-3) ion beam was irradiated on the SiO@sub 2@ surface at various incident angles. The noble gas ions, such as Ne@super +@, Ar@super +@, Kr@super +@, and Xe@super +@, were also irradiated to compare chemically active CF@sub x@@super +@ ions. The angular dependence of the etch yield depends on the kind of CF@sub x@@super +@ ion. In the case of CF@sub 3@@super +@ ion irradiated at 1 keV, the etch yield increases little with the incident angle below 60°, and decrease rapidly due to the reflection of the ion at the surface over 60°. The ratio of the etch yield at 60° to that of 0° is about 1.2. On the other hand, in the case of CF@sub 1@@super +@ ion at 1 keV, the etch yield increases rapidly with the incident angle below 60°. The ratio of the etch yield at 60° to that of 0° is about 2.3. In the case of the noble gas ions, the angular dependence of the etch yield does not depend on the species, indicating cos@super -2@@theta@ below 60°. The etch yields of CF@sub x@@super +@ ions were analyzed on the basis of an etching model, involving two components originated from different removal mechanisms. The chemical component, due to the thermally desorbed molecules generated through the chemical reactions between incident species and substrate materials, is constant with the incident angles. The physical component, due to the atoms sputtered away from the substrate by the momentum transfer through collision cascade, depends on the incident angle like cos@super -2@@theta@. This model can explain the angular dependence of the etch yields of CF@sub x@@super +@ ions at 1 keV very well. The chemical component of each CF@sub x@@super +@ ion is proportional to the number of the fluorine atoms in the ion with the coefficient of 1/2, consistent with the observation that SiF@sub 2@ is the main desorbed product. This work was funded by NEDO.

5:00pm **PS1-WeA10 Reactive Surface Coefficients for Radicals in a Vacuum Beam System**, ***Y. Kimura,*** *J. Coburn, D. Fraser, H. Winters, D.B. Graves,* University of California, Berkeley

We present direct measurements of reactive surface coefficients for various radicals on a range of surfaces. The reactive surface coefficients are determined using the Radical- and Ion-Surface Interaction Analysis System (RISIAS). RISIAS is equipped with two external radical sources and an external ion beam source, all of which can be simultaneously trained on a surface. A threshold ionization quadrupole mass spectrometer (TIQMS) is aligned with one of the radical beamâ€™s line of sight to measure radical flux in the beam. After measuring the radical flux, the TIQMS is vertically translated to allow insertion of a sample surface into the beam path via a load lock. With the sample surface in place, reflected radicals are measured with the TIQMS through a separate aperture. Choppers are used for background subtraction, allowing a direct measurement of the incident beam and reflected components. Experiments conducted with a temperature-controlled quartz crystal microbalance allow measurements of net deposition or etching with various beam components on a range of surfaces. The beam-to-background ratio of the radical beam in the TIQMS is measured to be 15 for the direct line of sight, and about 1 for reflected radicals. RISIAS can measure reactive surface coefficients from ~ 0.01-1. Measurements of CF@sub 3@, CF@sub 2@, CF, NH, NH@sub 2@, F and O radicals reacting with stainless steel, silicon, silicon dioxide, hydrocarbon and fluorocarbon surfaces will be presented.

Plasma Science and Technology
Room 315 - Session PS2-WeA

Atmospheric Plasmas & Micro Discharges

Moderator: G. Selwyn, Los Alamos National Laboratory

2:00pm **PS2-WeA1 Electrical Characterization and Time-resolved Emission Spectroscopic Studies of Dielectric-barrier Controlled Atmospheric-pressure Glow Discharges in Helium**, ***J. Shin,*** *P.L. Varghese, L.L. Raja,* The University of Texas at Austin

We report experimental studies of a dielectric-barrier controlled atmospheric-pressure glow (APG) discharge. The study is aimed at providing fundamental understanding APG discharge phenomena in high-purity helium. Electrical characteristics and time-resolved emission spectroscopic diagnostics are used. Dielectric barrier controlled APG discharge phenomena is characterized by a single or multiple current pulse during each half cycle of voltage input to the discharge. We study discharge phenomena under a variety of conditions such as varying gap sizes, operating frequencies and dielectric placement. Significant and random scattering as well as random asymmetries in current pulse shape are observed. We correlate these discharge peculiarities with the time-resolved emission spectroscopic results. In particular, we report spectroscopic observations of discharge condition just prior to glow-to-arc transitions.

2:20pm **PS2-WeA2 Measurement of the Fluorine Atom Concentration in a Carbon Tetrafluoride and Helium Atmospheric-Pressure Plasma**, ***X. Yang,*** *S.E. Babayan, G.R. Nowling, M. Moravej, R.F. Hicks,* University of California, Los Angeles

A titration technique has been developed to measure the fluorine atom concentration in the downstream region of a low-temperature, atmospheric pressure plasma fed with helium and carbon tetrafluoride. The fluorine atoms were titrated with H@sub 2@ molecules, and the HF reaction product was detected by infrared spectroscopy. The radio-

frequency gas discharge produced 1.2x10@super 15@ cm@super -3@ of F atoms, which was about two orders of magnitude higher than that found in low-pressure plasmas. The average electron density and temperature in the plasma was estimated to be 6.1x10@super 11@ cm@super -3@ and 2.5 eV. A numerical model of the plasma indicated that most of the fluorine atoms were generated by the reaction of CF@sub 4@ with metastable helium atoms. The results of the experiments and the model will be presented at the meeting.

2:40pm **PS2-WeA3 Generation Mechanism of the Atmospheric Glow in a DBD Configuration***, **E. Aldea,*** Eindhoven University of Technology, The Netherlands*; C.P.G. Schrauwen,* TNO-TPD , The Netherlands*; M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

Conventional wisdom attributes the generation of atmospheric glow plasmas to gas pre-ionization, which is related to ions or to electron generation by metastable-metastable and metastable-surface collisions . However there is not yet unambiguous experimental evidence, which can prove the validity of either of the proposed mechanisms. Beside that this pre-ionization mechanisms can not explain either how the glow to arc transition a notorious instability of atmospheric plasmas is avoided. Therefore to our opinion the physical basis of the atmospheric glow remains an open and challenging issue. In this contribution we analyze the basic conditions needed for uniform glow plasma generation. A simple analysis of the glow generation indicates that it is extremely improbable that the metastables or ions can have a significant contribution to glow generation via a pre-ionization mechanism. The low diffusion rate of ions and metastables excludes any mechanism of streamers or electron avalanches superposition. The preionization mechanism based on ions or metastables cannot also explain why the standard breakdown mechanism of atmospheric plasma streamer breakdown does not occur. Besides these theoretical arguments no evidence was found in the experimental current-voltage characteristics, plasma emission or breakdown voltage suggesting a significant pre-ionization or even the presence of a large amount of metastables. We conclude that the major problem in generation of atmospheric glow plasma is glow to arc transition. In this respect metastables are rather the problem for a stable plasma generation because their presence enhance the probability of stepwise ionization and glow to arc transition. The experimental data suggests that the surface of the dielectrics plays a major role in uniform and stable atmospheric glow plasma generation. The surface effect is probably due to a high secondary emission at the surface.

3:00pm **PS2-WeA4 Ultraviolet Emission Spectroscopy and Absorption Spectroscopy of CF@sub 2@ Radical in Chemical Vaporization Machining (CVM) Plasma Generated with High Speed Rotating Cylindrical Electrode***, **Y. Oshikane**, S. Sato, A. Nagao, K. Yamamura, K. Endo, Y. Mori,* Osaka University, Japan

Optical emission spectroscopy and broad-band absorption spectroscopy in UV region have been applied for determining CF@sub 2@ radical density in the chemical vaporization machining (CVM) plasma, which is generated in below 1 mm gap between the side of rotating cylindrical electrode (alumina) and flat substrate (silicon, quartz) by VHF at 150 MHz. By using a grating spectrograph consists of imaging aspheric mirrors coupled with cooled CCD camera, a spatially resolved UV spectrum has been recorded for CF and CF@sub 2@ radicals. Relative changes in CF@sub 2@ density in He/CF@sub 4@/O@sub 2@ plasma were monitored. The experiments cover a wide range of pressure, composition, rotation speed, and power deposition conditions (10@super 3@-10@super 5@ Pa, 0.01-1% CF@sub 2@, 0.01-1% O@sub 2@, 0-2000 rpm, 15-100 W). Increasing the pressure from 10@super 3@ to 10@super 5@ Pa showed large changes in CF@sub 2@ band spectrum. Both emission and absorption spectrum of a 10@super 3@ Pa He/CF@sub 4@/O@sub 2@ plasma showed the A(0,v,0)-X(0,0,0) (v=0 to 13) transition of the CF@sub 2@ molecule from 230 to 270 nm. But the spectrum shifts to longer wavelengths and showed the A(0,0,0)-X(0,v,0) (v=0 to 10) transition spectrum from 260 to 340 nm at atmospheric pressure. The spatially resolved absorption spectrum showed the absorption peaks near the side of electrode and substrate surface.

3:20pm **PS2-WeA5 A Simulation Study of the Role of Surface Phenomena in Dielectric-barrier Atmospheric-pressure Glow Discharges***, **X. Yuan**, L.L. Raja,* The University of Texas at Austin

Atmospheric-pressure glow (APG) discharges controlled by dielectric barriers can be used for a variety of new applications such as etching and deposition of thin films, surface modification, and plasma sterilization, without need for vacuum chambers. Dielectric-barrier controlled APG discharges exhibit a variety of interesting phenomena that are determined by plasma dynamics, volumetric chemistry, and dielectric surface effects. A clear understanding of these interactions is often difficult to unravel through purely experimental means and first principles simulation approaches can play an important role. In this talk, we will present detailed one-dimensional simulation results for a dielectric-barrier APG discharges in high-purity helium. Simulation results will be used to explain several experimentally observed dielectric-barrier APG characteristics such as large scatter in peak current values, asymmetry in current pulses, and parametric dependence of peak current pulse values on different discharge operating conditions. Our modeling results present convincing evidence that run-to-run variations in surface conditions (such as secondary electron emission coefficients) control the experimental observations such as scattered and asymmetric current pulses.

3:40pm **PS2-WeA6 Miniature Microwave Plasma Torch Applicators and Characteristics***, **T.A. Grotjohn,*** Michigan State University and Fraunhofer Center for Coatings and Laser Applications*; K. Hemawan, S. Zuo,* Michigan State University*; J. Asmussen,* Michigan State University and Fraunhofer Center for Coatings and Laser Applications

The experimental evaluation of two miniature microwave plasma torch applicators that have potential use in materials synthesis and surface treatment are described. The first applicator employs an open ended coaxial structure with the discharge located at the tip of the center conductor. The discharge is formed at atmospheric or slightly below atmospheric pressure where the feed gas flows through the center conductor of the applicator. The second applicator is similar to a microstripline coupling structure described earlier.@footnote 1@ This applicator couples microwave energy to a surface wave discharge formed in an open ended tube placed between and perpendicular to the strip transmission lines. The feed gases are fed directly through the surface wave discharge and flow out to a pressure controlled environment ranging from approximately 10 Torr to atmospheric pressure. Both microwave plasma torches are experimentally evaluated over a range of input power and a variety of feed gas mixtures including argon, mixtures of argon with hydrogen and selected hydrocarbon gases, nitrogen, and air. These torches operate from 10's to 100's of watts of input power and are able to maintain discharges over a wide range of flows from diffusional flow of radicals for gentle surface processing to high velocity flows approaching supersonic velocities. Objectives of this work are to create compact microwave plasma torch designs that operate from below atmospheric pressure to one atmosphere pressure with processing spot sizes ranging from several mm down to less than 0.25 mm. The numerous applications of these microplasma torches include cutting, welding, cleaning and other surface treatments. @FootnoteText@ @footnote 1@ T. A. Grotjohn, et.al., "Characteristics of Miniature Microwave Excited Plasma Discharges," AVS Symposium, Denver, 2002.

4:00pm **PS2-WeA7 Microplasma Surface Modification of the Inner Surface of Small Diameter Polyethylene Tubing for Improved Hematocompatibility***, **J.L. Lauer**, J.L. Shohet, C. Pratoomtong, R.D. Bathke, R.M. Albrecht, S. Esnault, J.S. Malter,* University of Wisconsin, Madison*; S.B. Shohet,* University of California, San Francisco*; U. von Andrian,* Harvard Medical School

Microplasma surface modification was used to modify the inner surface of small diameter (280 and 800 µm and up to 1 meter in length) polyethylene (PE) tubing. Polyethylene glycol was grafted to the lumenal surface using an oxygen plasma and then cross-linked with an argon plasma. The plasma was created by placing hollow cathodes electrodes, in vacuum, at the ends of the PE tubing. The electrodes were powered by a 15 kV pulsed a.c. supply. Since feedstock gases and reaction products must pass along the length of the tubing, the resulting pressure drop has the potential to cause nonuniform plasma chemistry and thus a nonuniform treatment along the tubing. Emitted light from the plasma was analyzed with a monochromator, that was moved along the length of the tubing, giving insight on plasma uniformity. Treatment effectiveness on the lumenal surface was evaluated using a capillary rise method, which can be directly related to the contact angle. Uniformity of the atomic surface composition along the length of the inner surface of the PE tubing was analyzed by XPS. To test for hematocompatibility, a loop, powered by a peristaltic pump, circulated heparinized human blood for times up to one hour at flow rates of the order of 1 ml/minute at 37 C. After the flow test, the tubing was rinsed with phosphate buffer solution (PBS) for 10 minutes (with the same flow rate as the blood). The cells were fixed for 30 minutes with 1.25% by volume glutaraldehyde and 0.5% by weight tannic acid dissolved in PBS. After the fixation, the tubing was rinsed with PBS for another 10 minutes. It was then dehydrated with two-minute exposures to ethanol of increasing

concentration from 50% to 95%. Plasma-treated and untreated tubing were then evaluated by studying the morphology of adhering platelets along the tubing with SEM. By suitably modifying the plasma parameters, the degree of uniformity as a function of distance along the tubing and proximity to the peristaltic pump can be optimized.

4:20pm **PS2-WeA8 Microdischarge Plasma in Supercritical Fluid*, K. Terashima,*** The University of Tokyo, Japan **INVITED**

We have performed the study of microscale/nanoscale plasma science and technology.@footnote 1@ In this talk, our recent work on microdischarge plasma in supercritical fluid (SCF), particularly near the critical point (CP), for CO@sub 2@ (CP:7.38MPa,304K)and H@sub 2@O (CP:22.1MPa,674K), are presented. SCF,which is an intermediate state of matter between liquid and gas, has attracted much interest in scientific and enginering fields due to abnormal characteristics, such as high solubility. In particular, near CP, large density fluctuation results in drastic change of the properties. From a microscopic viewpoint, the SCF consistes of various sized clusters. Therefore, it is highly anticipated that the ionized state, such as the plasma state, in SCF may exhibit unique characteristics and reactions, that are distimct from those of the normal plasma state in gas. In addition to the first generation@footnote 2@ of plasma in SCF, abnormal features of breakdown voltages (V@sub B@) as a function of environmental pressure are demonstrated. For CO@sub 2@, measurements of V@sub B@as a function of pressure for high-pressure CO@sub 2@ up to SCF conditions of various temperatures have been performed using a 1-µm-gap coplanar film electrode. The curve of the V@sub B@ exhibits an inflection at around 3 MPa and a drastic decrease near CP. The V@sub B@ in pressure environments higher than the inflection at around 3 MPa can be analyzed using the Townsend theory and density fluctuations, which typical indicates clustering, and the drastic decrease of V@sub B@ near CP was shown by a scaling function. The same features were also observed for H@sub 2@O. Finally, as an example of an application, the preparation of carbon-cluster systems, such as nanopolyhedra and nanotubes, using SCF-CO@sub 2@ plasma is also presented. @FootnoteText@ @footnote 1@ K.Terashima, L.Howald, H.Haefke and H.J.Güntherodt, Thin Solid Films 282(1996)634. @footnote 2@ T.Ito and K.Terashima, Appl.Phys.Lett.80(2002)2854.

5:00pm **PS2-WeA10 Two-dimensional Simulation of dc Microdischarge Phenomena*, P.S. Kothnur,*** *L.L. Raja,* The University of Texas at Austin

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. Recently, arrays of microhollow cathode discharges are being investigated for applications such as sources of flat panel light sources or electron sources. While some estimates of properties of micro hollow cathode discharges are available, a detailed understanding of the plasma dynamics and chemistry is lacking. Further, it is not fully clear as to what conditions influence the existence of the hollow cathode effect in microdischarge geometries. This talk presents results from a self-consistent, two-dimensional computational study of the glow-like phenomena in microdischarges. The model includes a description of multi-species transport and chemistry, electric field, electron and heavy species energy distributions in the microdischarge. The talk explores conditions under which the hollow cathode effect occurs in microdischarge geometries, and presents a fundamental understanding of the overall microdischarge phenomena. Further, we explore thermal heating effects in dc microdischarges in the presence of bulk flow inside the discharge. This aspect of the study is motivated by our proposed use of microdischarges in space thruster applications.

Plasma Science and Technology
Room 314 - Session PS1-ThM

Plasma-Surface Interactions: Deposition

Moderator: S.M. Han, University of New Mexico

8:20am **PS1-ThM1 Reactive Sputtering of Metallic Tin in a Mixture Ar - O2 : Comparison between an Amplified and a Classical Magnetron Discharge***,* ***R. Snyders,*** Mons-Hainaut University, Belgium

Industrially, magnetron sources are widely used for coating and surfaces treatments. The problem encountered by "classical" magnetron sputtering is the shadowing effect when complex substrates have to be treated. Neutral particles arrive on the substrate surface with a broad angular distribution of trajectories and as a consequence the deposited film is of poor quality. Ionizing the sputtered particles can solve this problem. Velocity control and normal trajectory of the ionized species can be achieved by applying a bias voltage to the substrate. For that purpose, a R.F. (13.56 MHz) power supplied copper coil (diameter of 4 cm) has been set up, between the DC tin magnetron target and the substrate holder. The applied R.F. power used to create the secondary plasma can be raised up to 200 W. The aim of this work is to estimate the RF coil influence on the chemical behaviour of both the discharge and the films during the deposition of SnOx thin films in a mixture Ar - O2. During the deposition, the discharge is characterized by the target voltage, the deposition rate and glow discharge mass spectrometry whereas the prepared films compositions are obtained from in-situ XPS measurements. During the work, we have observed the influence of both the gas mixture composition and the RF power on the discharge and on the films. By increasing the RF power on the coil, we have observed on both the plasma and the films compositions an increase of the oxidation level for the same ratio O2 / Ar. On the other hand, the metal â€“ compound transition at the target, observed on the discharge voltage and on the deposition rate measurements are not influenced by the coil. So, using the RF coil the films oxidation can be reached at lower reactive gas flow and consequently at higher deposition rate.

8:40am **PS1-ThM2 Selective Plasma-induced Deposition of Fluorocarbon Films on Metal Surfaces for Actuation in Microfluidics***, P. Bayiati,* ***A. Tserepi****, E. Gogolides, K. Misiakos,* National Center for Scientific Research (NCSR) "Demokritos", Greece

Plasma-induced deposition of polymer films on surfaces is an important issue in etching plasmas, since on one hand it allows selective etching of materials,@footnote 1@@footnote 2@ while on the other it provides side wall passivation necessary for anisotropic high-aspect ratio etching. The present work focuses on the selective deposition of fluorocarbon (FC) films on metal surfaces, specifically on aluminum, over SiO@sub 2@ surfaces, in order to obtain surfaces of distinct wettability. If, in addition, the wettability of the modified metal surface can be controlled electrostatically and consequently the surface be varied from a hydrophobic to a hydrophilic one, such plasma-modified metal surfaces can be used as electrodes employing electrowetting for actuation of fluid transport in microfluidic devices.@footnote 3@ Since polymer layers on surfaces are easily formed in fluorocarbon discharges with high concentrations of radical CFx species, fluorocarbon gases such as C@sub 4@F@sub 8@ and mixtures of CHF@sub 3@/CH@sub 4@ were used in our experiments. For the selection of conditions appropriate for selective deposition of FC films on Al over SiO@sub 2@, plasma parameters such as plasma power, bias voltage, electrode temperature, and gas composition were varied. The wettability of SiO@sub 2@ and Al surfaces exposed to FC plasmas under different plasma deposition conditions was characterized by contact angle measurements (without and with voltage application). Contact angles as a function of the applied voltage were used to yield the thickness of the FC film deposited on Al, and to indicate the breakdown voltage for the films under consideration. The results demonstrate the feasible use of such plasma-deposited films on Al for electrostatic actuation with application of relatively small voltages (less than 10 V). @FootnoteText@ @footnote 1@G. Oerlein, Surface Science 386, 222 (1997); and G. Oerlein et. al., J.Vac. Sci. Technol. A 12(2), 333 (1994).@footnote 2@L.Rolland, M.C. Peignon, Ch. Cardinaud, G. Turban, Microel. Engin. 53, 375 (2000).@footnote 3@M. Pollack, R. Fair, A. Shenderov, Appl. Phys. Lett. 77(11), 1725 (2000).

9:00am **PS1-ThM3 Deposition of Transparent Tin Oxide Films by PECVD on Polymers***,* ***F. Arefi-Khonsari****, J. Pulpytel,* Laboratoire de Genie des Procedes Plasma et Traitement de Surface ENSCP, France*; H. Cachet,* UPR15-CNRS, France **INVITED**

Transparent conductive tin oxide films have been deposited at low temperature(< 50°C) from a mixture of O@2sub@/Ar/TMT on two substrates for two different applications : 1) biofouling reduction for underwater instrumentation on polymer windows and 2)as sensitive layers of gas microsensors on silicon wafers. In order to obtain carbon free tin oxide films, mass spectrometry was performed by using a calibration mixture composed of inert gases. The latter allowed us to determine the molar fraction of the stable species produced in the discharge, such as CO & CO@2sub@ namely those which witness the carbon etching of the organometallic precursor. For this study the role of the two major parameters i.e. power and oxygen partial pressure in the reactor have been studied. The biofouling reduction was based on seawater electrolysis at the optical surface for producing active chlorine species. In order to limit the ageing effect of tin oxide films deposited on polymers, they were doped with fluorine atoms which gave rise to higher conductivities and limited also the ageing effect. Precursors such as SF@6sub@ and C@4sub@F@6sub@ were introduced in the plasma mixture in order to dope the tin oxide films in a one step process. In the case of SF@6sub@, an increase of the electrical conductivity and charge carriers were obtained for very small flow rates of SF@6sub@ introduced in the discharge. For higher flow rates, a sharp decrease of the conductivity was observed. For such flow rates, competitive etching and functionalization processes, assisted by fluorine atoms present in the discharge, took place giving rise to a sharp decrease of the deposition rate and the incorporation of Sn-F and C-F bonds in the deposited films. This has been explained by the formation of new species such as S O@2sub@, SOF, SOF@2sub@ and HF. Oxygen being consumed to form such species, it is much less involved in forming CO, CO@2sub@ and H@2sub@O species, therefore leading to the incorporation of carbon species in the deposit which explains the sharp decrease of the conductivity of the films.

10:20am **PS1-ThM7 Temperature Dependence of the SiH@sub 3@ Surface Reactivity During Plasma Deposition of a-Si:H Studied by Time-resolved CRDS***,* ***J.P.M. Hoefnagels***[1]*, Y. Barrell, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

The surface reactivity of SiH@sub 3@ - the dominant radical during deposition of hydrogenated amorphous silicon (a-Si:H) from SiH@sub 4@ plasmas - has been investigated to obtain information on the elemental surface reactions during a-Si:H film growth. To do so, we have measured the surface reaction probability @beta@ of SiH@sub 3@ for substrate temperatures in the range of 50-450 °C by means of the novel time-resolved cavity ringdown spectroscopy (@tau@-CRDS) method. In this method, the highly-sensitive CRDS absorption technique is used to map the temporal decay of the SiH@sub 3@ radical density (probed at the Ã@super 2@A@sub 1@'<-@td X@@super 2@A@sub 1@ transition) after a minor periodic modulation of the density during regular plasma operation. From measurements of the SiH@sub 3@ loss time versus the SiH@sub 4@ partial pressure, it has been verified that SiH@sub 3@ is not lost by gas phase reactions, as is, e.g., the case for the Si radical. The surface reaction probability of SiH@sub 3@ has been deduced for different substrate temperatures from the pressure dependence of the SiH@sub 3@ loss time using information on the gas temperature and the diffusion of SiH@sub 3@ towards the surface. The gas temperature - determined from Doppler broadening of Si absorption lines - is ~1500 K and is unaffected by the substrate temperature. This procedure has revealed that the surface reaction probability of SiH@sub 3@ is independent of the substrate temperature with a value of @beta@=0.30±0.03. For comparison, the surface reaction probability of Si has been determined for 200 °C and is very close to unity (0.95<@beta@@<=@1). These observations will be discussed in terms of the contribution of different plasma radicals to film growth and the possible SiH@sub 3@ surface reactions taking place. The results suggest a two-reaction step growth mechanism for a-Si:H with a temperature-independent abstraction reaction of H from the surface as the rate-limiting step.

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

10:40am **PS1-ThM8 Creation of SiOF Films with SiF@sub 4@/O@sub 2@ Plasmas: from Gas-Surface Interactions to Film Formation***, J. Zhang, E.R. Fisher,* Colorado State University

Fluorinated SiO@sub 2@ (SiOF) films have been studied because of their relatively low dielectric constant and their potential as a replacement for SiO@sub 2@ in the microelectronics industry. Despite the intense scrutiny, many of the details of the mechanisms for SiOF film deposition remain unclear. Here, we deposited SiOF films using SiF@sub 4@/O@sub 2@ plasmas. The plasma parameters of SiF@sub 4@ percentage in the feed gases (%SiF@sub 4@) and applied rf power (P) were studied as well as the effects of ion bombardment and substrate temperature on film deposition. Fluorine incorporation in the film increases with increasing %SiF@sub 4@ and P. Film deposition rate also increases with P, whereas its dependence on %SiF@sub 4@ is more complex. Ion bombardment decreases the film deposition rate and affects film composition significantly. On the molecular level, we examined the surface reactivity of SiF and SiF@sub 2@ during SiOF film deposition using the imaging of radicals interacting with surfaces (IRIS) technique. SiF shows high surface reactivity, R, which varies from 0.95 ± 0.08 to 0.60 ± 0.07, depending on plasma parameters. In contract, SiF@sub 2@ shows significant surface production. The scattering coefficient, S, varies from 1.12 ± 0.08 to 2.52 ± 0.16. The surface interactions of SiF and SiF@sub 2@, along with plasma gas-phase composition, were correlated with film characteristics to reveal the possible film-deposition processes.

11:00am **PS1-ThM9 Study of Fluorocarbon Deposition Mechanism with a Small Gap Structure in Fluorocarbon Plasmas***, L. Zheng, X. Li, X. Hua, L. Ling, G.S. Oehrlein,* University of Maryland, College Park*; E.A. Hudson,* Lam Research Corp.

We designed a small gap structure to study the deposition of fluorocarbon film in a high aspect ratio feature in an inductively coupled rf plasma (ICP) reactor in an effort to provide information on fluorocarbon film formation mechanisms for highly selective dielectric etching processes. The small gap structure exhibits three regions for fluorocarbon film formation: A region exposed to the full plasma, transition region and a completely shadowed region where only long-lived species can arrive after multiple collisions with the walls. Both in situ (real time) and external He-Ne ellipsometers were used to monitor the deposition rate of the fluorocarbon film on the base wafer. X-ray photoelectron spectroscopy (XPS) was used to analyze the detailed surface chemistry of the fluorocarbon film. CFx (x = 1-3) radicals produced in fluorocarbon discharges act as precursors for the formation of fluorocarbon film. Effects of different gases (C4F8, C4F6), Ar addition, gap height, pressure on refract index and deposition rate of the fluorocarbon film in the three regions were studied and a simple model based on Knudsen diffusion mechanism was developed to describe the fluorocarbon film deposition in the completely shadowed region. We also will describe an equivalent set of studies performed in a 40 MHz (source power) - 13.56 MHz RF (bias power) dual frequency capacitively coupled system.

11:20am **PS1-ThM10 Plasma Chemistry and the Growth Kinetics of Silicon Nitride Deposited by the SiH@sub 4@-N@sub 2@ Reactant Mixture***,* ***F.J.H. Van Assche****, J. Hong, M.C.M. van de Sanden, W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands

Plasma ions and radicals in a remote plasma operated on an Ar-H@sub 2@-N@sub 2@-SiH@sub 4@ mixture have been studied by several diagnostics such as Langmuir probe measurements, ion mass spectrometry, cavity ringdown spectroscopy, and threshold ionization mass spectrometry. It is shown that the H radicals that emanate from the plasma source react with the SiH@sub 4@ admixed downstream and create a high SiH@sub 3@ density. Si and SiH radicals have also been measured but they have a much lower density in the downstream plasma. Ground-state N radicals emanating from the plasma source do not react with the SiH@sub 4@ injected downstream leading to a high N density under the silicon nitride deposition conditions. This has lead to the conclusion that N and SiH@sub 3@ radicals dominate the silicon nitride growth process as has also been confirmed by the correlation between the SiH@sub 3@ and N density in the plasma and the incorporation flux of Si and N atoms into the silicon nitride films. Furthermore, from this correlation very reasonable sticking probabilities of the N and SiH@sub 3@ radicals have been obtained. >From these results, the following kinetics for silicon nitride growth from the N@sub 2@-SiH@sub 4@ reactant mixture are proposed: During deposition an amorphous silicon-like surface layer is created by the SiH@sub 3@ radicals and simultaneously this amorphous silicon-like surface layer is nitridated by the N radicals leading to silicon nitride formation. Further support for this mechanism is obtained by experiments in which silicon nitride films have been created by exposing amorphous silicon films to a high flux of N radicals.

11:40am **PS1-ThM11 Molecular Dynamics Simulations of Organic Polymer Etching by H@sub 2@/N@sub 2@ and NH@sub 3@ Plasmas***, H. Yamada, S. Hamaguchi,* Kyoto University, Japan

Using classical molecular dynamics (MD) simulations, plasma-surface interactions have been investigated for organic polymer etching processing with H@sub 2@/N@sub 2@ and NH@sub 3@ plasmas. To perform MD simulation in such systems, we have developed an interatomic potential model applicable to systems consisting of H, C, and N atoms [i.e., (H,C,N) systems]. Further we have also worked with the Abel-Tersoff-Brenner (ATB) potential proposed for (H,C) systems. Reducing the dielectric constants of insulating materials for interconnect circuits is of significant importance for the manufacturing of fast computer chips based on the copper wiring. For this purpose, organic polymers with low dielectric constants (i.e. low-k) have been studied recently as an alternative to SiO@sub 2@. In addition to such use, organic polymers have been studied for other applications, for example, substrates of healthcare chips and optical waveguides. Hydrogen and nitrogen based plasmas such as N@sub 2@+H@sub 2@ or NH@sub 3@ plasmas are often used to etch such polymer surfaces with micron and submicron structures. The goal of this work is to study plasma-surface interactions of polymer etching process, using classical MD simulations. To represent surface reactions correctly, it is critical to employ realistic interatomic potential functions for MD simulations. In this work, therefore, we present interatomic potential functions for (H,C,N) systems, extending the Stillinger-Weber potential with some modification such as the inclusion of double and triple bonds. To compare simulation results with our potential model with those with other potential models, we have also run MD simulations with the ATB potential. Because many low-k organic polymers contain Benzene-like rings, we use poly (1,4-phenylene) as our model substrate. Preliminary results of the MD simulations will be presented.

Plasma Science and Technology
Room 315 - Session PS2-ThM

Low k Dielectric Etch

Moderator: R. Turkot, Intel Corporation

8:20am **PS2-ThM1 Smart Nanoprocess for Organic Low-k Film Etching***,* ***M. Hori****,* Nagoya University, Japan **INVITED**

Conventional plasma etching process depends on the external parameters such as gas pressure and input power, and hereby the optimal process condition must be obtained by investigating etching characteristics for each process. On the other hand, smart nanoprocess, where both etching rate and pattern profile are controlled with the assistance of feedback system based on the information of species monitored in situ, will enable us to realize the high performance in nano-scale fabrication. In this study, we have focused on monitoring the behavior of radical densities in the plasma to understand gas phase and subsurface reactions of radicals. By choosing internal parameters of densities (radicals and electrons) and a substrate temperature, both etching rate and fine pattern profile were controlled precisely. The behavior of species in the gas phase and their effects on the etching characteristics of organic low-k film were investigated in 500 MHz ultrahigh frequency (UHF) plasma and 13.56 MHz inductively coupled plasma using N@sub2@/H@sub2@ and N@sub2@/NH@sub3@ gas chemistry. The absolute H and N radical densities were measured by vacuum ultraviolet absorption spectroscopy employing a very compact light source. The vertical profile with a high etch rate of about 400 nm/min was successfully obtained in both plasmas simply by choosing a radical density ratio of H/H+N=0.8 and a substrate temperature of 20°C. The time evolution of plasma-induced subsurface reaction for the vertical profile was observed by Fourier transform infrared attenuated-total-reflection (FT-IR ATR) and in-situ XPS. Furthermore, the fundamental etching mechanism was clarified using multi-beams of ions and radicals. It is indicated that the smart nanoprocess is promising for the precise etching of organic low-k films.

9:00am **PS2-ThM3 Etching Mechanisms of Methylsilsesquioxane Low-k Material in High Density Fluorocarbon Plasma***,* ***D. Eon****, V. Raballand, G. Cartry, M.C. Peignon-Fernandez, C. Cardinaud,* CNRS, University of Nantes, France

At present, performances in integrated circuit (IC) are limited by interconnection delay, which increases with the reduction of feature size

(below 100 nm). One solution to reduce interconnection delay, is to diminish the parasitic capacitance between levels by replacing SiO_2 (k=4.5) conventional interlevel dielectric by a low dielectric constant material (low-k). The integration of these into IC fabrication requires i) that a selective etching is achievable with respect to the mask and bottom layer ii) that the etching does not adversely affect the permittivity of the film. This study concerns the etching of the methylsilsesquioxane based materials (SiOC k=2.9, SiOC with 40% of porosity k=2.2) and compared to SiC etch stop layer (k=4.5), with the aim to investigate etch mechanisms. We used a 13.56 MHz Inductively Coupled Plasma source mounted above a diffusion chamber where the substrate is biased separately. Etch rates are measured in real time by in-situ multi-wavelength ellipsometry. Surface composition is analysed by quasi in-situ XPS. Langmuir probe is used in order to determine plasma densities, ion flux, and electronic distribution. Mass spectrometer and optical emission spectroscopy measurements are carried out to obtain chemical composition of the plasma. Etching has been performed in C_2F_6 in mixture with H_2, Ar, N_2, or O_2. According to these results, we studied thoroughly the mixture C_2F_6/H_2 (25%/75%), which gives the best compromise between selectivity and etch rate. For all materials and conditions, the etch rate and the atomic F concentration are strongly correlated. On another hand, XPS shows that CF_x species, when present, play an important role on the etching mechanism of SiC and SiOC. Conclusion is that selective etching requires to control precisely the formation of the passivation layer.

9:20am **PS2-ThM4 Low Damage Low-k Film Etching using Advanced Neutral Beams**, ***H. Ohtake***, *N. Inoue, T. Ozaki, S. Samukawa,* Tohoku University, Japan

Low damage processes on the porous MSQ by using neutral beam were investigated. The porous MSQ is very vulnerable to the plasma exposure. Especially, the methyl is drawn out from the porous MSQ during the ashing process, which causes the increase of dielectric constant. In this paper, we investigated the application of the neutral beams to the ashing processes without the effect of ions and photons. In oxygen beam, we observed the increase of the dielectric constant of low-k film as much as that in the oxygen plasma. However, when we used the hydrogen beam, the MSQ dielectric constant did not change while it increased in the case of hydrogen plasma. According to the XPS analysis, it was found that the modified layer of carbon hydride is generated on the surface of porous MSQ by hydrogen beam exposure. This modified layer is thought to prevent the methyl from being drawn out from the porous MSQ. On the other hand, in the hydrogen plasma, it is thought that the generation of this modified layer is restricted by the photons or the ions. In addition, when we used the gas mixture beam of hydrogen and nitrogen, the modified layer of carbon nitride is generated on the surface of MSQ. This layer also prevents the methyl extraction from the porous MSQ. Accordingly, the low damage ashing-processes can be achieved by using hydrogen or hydrogen- nitrogen beam because of the generation of the modified layer.

9:40am **PS2-ThM5 Control of Degradation Thickness on SiOCH Surface**, ***T. Tatsumi***, *T. Saitoh, A. Ando, K. Nagahata, Y. Morita,* Sony Corporation, Japan

We investigated ashing technologies for low-k/Cu integration. SiOCH film oxidizes easily forming a degradation layer that must be minimized to suppress the CD variations during wet treatment. We used an ashing system using ICP and evaluated the ashing rate, residue, and the thickness of the damaged layer (T_d) on the side-wall of the SiOCH via hole. When we used H-based plasma for ashing, T_d was relatively thin. However, it was difficult to maintain a high etch rate and to remove the residue completely. Hence, we had to use O-based gas chemistry in mass production. Using O_2 plasma, T_d depended on (a) the O radical density, (b) the thickness of the C-F polymer formed on the sidewall during via etching, and (c) wafer temperature. The density of O radical depended on the partial pressure of O_2 and dissociation degree of O_2, which could be related to the number of collision with electrons: $N_e<\sigma v>$, where N_e, σ, and v were electron density, collision cross-section for dissociation, and electron energy, respectively. We estimated $N_e<\sigma v>$ from the intensity of the optical emission of Ar (750 nm, $I_{Ar}=N_{Ar}N_e<\sigma v>$) and we found that the ashing rate, as well as the thickness of the damaged layer under various conditions, clearly depended on the "partial pressure of O_2" x "I_{Ar}/N_{Ar}". When we minimized the radical density by using low density (< 6 x 10 cm^{-3}) and low pressure (< 3Pa) conditions, the thickness of the damaged layer could be suppressed below 10 nm while the ashing rate was higher than 500 nm/min with no residue. To fabricate reliable Cu interconnects, we not only need to etch various low-k materials, but also quantitatively control the degradation of these materials.

10:00am **PS2-ThM6 Three-dimensional Feature Profile Evolution during Etching of Porous Dielectric Materials**, ***Y.H. Im***, *M.O. Bloomfield, T.S. Cale,* Rensselaer Polytechnic Institute

Porous materials are being widely investigated for use as low dielectric constant materials for state-of-the-art integrated circuit (IC) interconnects. The patterning of these materials is one of the current challenges to be overcome for application to next generation ICs. Although conventional etching technologies can be used for this purpose, one of the barriers in adapting them to these materials is the lack of the fundamental understanding of how the complicated etching mechanisms interact with the inherently 3D structure of porous materials. It is desirable to employ 3D computer simulations to answer questions that cannot be addressed by 2D simulators. We present a fully 3D simulation study of feature topography evolution under various etching processes. As a part of this effort, we have used the parallel levelset environment for nanoscale topography evolution (PLENTE) to track the evolution of systems in 3D. PLENTE is used with the ballistic transport and reaction based process simulator EVOLVE, which in turn uses a 3D Monte Carlo view factor code, to predict the fluxes and coverages of chemical species on the evolving substrate. We compare the shape of etched feature profiles to experimental data for porous dielectric materials. Etch rate and feature profile evolution were examined as functions of process conditions and porous material properties such as porosity and average pore size. This simulation technique is designed to help process engineers understand new phenomena observed in etching of porous dielectric materials and smooth the adaptation of conventional etching recipes to porous substrates.

10:20am **PS2-ThM7 Etching of a Porous SiOC with Varied Porosity in Fluorocarbon Based-plasma**, ***N. Posseme,*** STMicroelectonics, France*; T. Chevolleau, L. Vallier, O. Joubert,* CNRS/LTM, France*; I. Thomas-Boutherin,* STMicroelectronics, France

In CMOS technology, the traditional SiO_2 is being replaced by Low-k materials in order to reduce the total resistance capacitance delay in the interconnect levels. Before Low-k materials can be implemented successfully, many problems must be solved such as the materials stability during etch and stripping processes. This work focuses on the etching of porous methylsilsesquioxane (MSQ) materials (spin on SiOC, k = 2.2) with different porosity (30%, 40% and 50%) in fluorocarbon based plasmas (CF_4/Ar). The surface and bulk modification after partial etching is studied using different surface analysis techniques such as quasi in-situ X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (FTIR), mercury probe capacitance measurement (C-V) and spectroscopic ellipsometry. The etching of these materials is performed on blanket wafers in a Magnetically Enhanced Reactive Ion Etcher. Similarly to non porous SiOC materials, a decrease in etch rate of porous SiOC films is observed with either increasing Ar dilution or polymerizing gas addition (CH_2F_2) leading in this last case to an etch stop phenomenon. The etch rate increases with higher porosity in the SiOC film, since less material per unit thickness need to be removed as the porosity increases. After partial etching, FTIR analysis indicate that the remaining film is altered by the direct impact of ion bombardment that induces a physical degradation of porous SiOC. This film modification increases with the amount of porosity in the film. The XPS results indicate that the interaction layer formed at the film surface has almost the same composition whatever the porosity of the films studied. Complementary study, from angle resolved XPS analyses reveals also that the C and F atoms diffuse inside the pores of the different films and induce bulk modification observed on FTIR spectra. XPS analysis are also conducted on the porous SiOC sidewalls using the chemical topography analysis technique.

10:40am **PS2-ThM8 In-situ Real-time Monitoring of Profile Evolution During Plasma Etching**, ***H. Gerung***, *C.J. Brinker, S.R.J. Brueck, S.M. Han,* University of New Mexico

We have employed attenuated total reflection Fourier transforms infrared spectroscopy (ATR-FTIRS) to monitor profile evolution during etching of mesoporous low-k SiO_2 film in-situ and real time. The porous SiO_2 films, stacked with anti reflective coating (ARC) and 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, and

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 have extended this technique to etching Ge. The results from Ge etching will be also discussed.

11:00am **PS2-ThM9 Critical Issues in Dual Damascene Etch***, **M. Hussein,** M. Heckscher, S. Suri,* Intel Corporation

This work examines the critical etch issues facing dual damascene integration scheme for the 90nm technology node and beyond. Emphasis will be placed on selectivity needs during via and etch stop layer etch, in particular. We investigated etching chemistries containing fluorine, and fluorocarbon-generating radicals using 300mm wafer size substrate. We will present and discuss the impact of chemistry and etching system configuration on etch selectivity during via and etch stop layer etch. Attaining a manufacturable level of selectivity between silicon-based low-k ILDs and advanced etch stop layers, in spite of the similarities in composition and characteristics of these materials, is shown to be quite challenging.

11:20am **PS2-ThM10 In-Situ Etch-Stop Etch for Cu/Low-k Damascene Etch Applications***, **P. Jiang**, R. Kraft, E. Burke,* Texas Instruments

An in-situ plasma etch process was developed for the 90nm technology in which damascene structures (vias or trenches) and their etch-stop layers are etched in a single chamber. The in-situ process sequence includes BARC opening, low-k dielectric (OSG) etch with high selectivity to etch-stop layer (SiC), and SiC etch-stop removal. This process has provided significant cost reduction and productivity benefits to the Cu single damascene integration schemes, due to fewer process steps and higher process yield. Preserving feature CDs and etch profiles for low-k dielectric etches with 193nm lithography is particularly challenging due to the poor etch resistance of 193nm resists and small CDs (<150nm). The in-situ process has reduced via etch CD bias by ~15nm as compared to the conventional ex-situ etch-stop etch. It has also eliminated via profile bowing induced typically by ex-situ etch-stop etch and post-etch cleans, and increased the selectivity of SiC to OSG by ~80% in the etch-stop etch step. More importantly, equivalent or better via yield was achieved with smaller CDs using the in-situ process, due to improved profiles. In this paper, we will discuss the development of in-situ etch-stop etch process for single damascene via etch. The detailed results about the process, and its impact on process and electrical performance will be reported.

11:40am **PS2-ThM11 Study of CO addition to C_4F_8 or C_4F_8/Ar Plasmas for Selective Etching of Organosilicate Glass (OSG) over SiC***, **L. Ling**, G.S. Oehrlein, X. Hua, X. Li,* University of Maryland, College Park*; F.G. Celii, K.H.R. Kirmse, P. Jiang,* Texas Instruments

We have examined the effect of CO addition to C_4F_8 or C_4F_8/Ar plasmas for selective etching of organosilicate glass over SiC etch stop layers. The variation of important gas phase species, thin film etching rates and surface chemistry with feedgas composition was determined. CO addition exhibits dramatically different consequences on OSG/SiC etching selectivity when added to either C4F8 or C_4F_8/Ar plasmas containing a high proportion of Ar (greater 80%). An improvement of the OSG/SiC etching selectivity results from CO addition to C_4F_8. Our data indicate little CO dissociation in this case, which is plausible considering the lower dissociation energy threshold of C_4F_8 relative to CO. X-ray photoelectron spectroscopy (XPS) analysis of OSG and SiC surfaces shows that the etching selectivity improvement for C_4F_8/CO may be explained by some incorporation of CO into deposited fluorocarbon films, an increase of the thickness and a reduction of the F/C ratio of the steady-state fluorocarbon surface layer on the SiC surface during etching. Adding CO to C_4F_8/90%Ar discharges leads to a reduction of the OSG/SiC etching selectivity. Significant dissociation of CO in Ar-rich C_4F_8/Ar/CO discharges is observed, consistent with the fact that the dissociation energy threshold of CO is lower than the Ar ionization and metastable energies. Oxygen incorporation in deposited fluorocarbon films and a reduction of the steady-state fluorocarbon surface layer thickness on SiC are observed by XPS in this case, explaining the loss of OSG/SiC etching selectivity for C_4F_8/Ar/CO discharges.

Plasma Science and Technology
Room 315 - Session PS-ThA

Plasma Diagnostics: Mechanisms

Moderator: N.C.M. Fuller, IBM TJ Watson Research Center

2:00pm **PS-ThA1 In-Situ Monitoring of Unstable Neutral Molecules using Ion Attachment Mass Spectrometer**, ***Y. Shiokawa***, *M. Nakamura, Y. Hirano, Y. Taneda, T. Fujii,* Anelva Corporation, Japan

Ion Attachment Mass Spectrometer (IAMS)@footnote 1@ has a unique advantage of fragment-free; mass analysis of true original molecule without dissociation, which is impossible by common methods such as electron impact. Therefore, IAMS has been expected to measure unstable neutral molecules in gas processes, and was already applied to analysis of thermal reaction by metallic-organic material for Cu-CVD and of exhaust gas from dry etching system.@footnote 2@ Although conventional IAMS used in these experiments is large and needed higher pressure than 100Pa for sampling, newly developed IAMS@footnote 3@ is compact and needs only 1Pa, so that IAMS in-situ monitor seems to be realized. Therefore we are investigating capabilities of new IAMS for in-situ monitoring of unstable neutral molecules in many processes, including tool for plasma diagnostics. In this experiment, plasma was produced by small inductively coupled source with 2Pa of c-C_4F_8 (100%), and new IAMS was put on it at a distance of 10cm apart. Neutral molecules of CF_2, C_2F_4, COF_2 by IAMS and ions of CF_2^+, $C_2F_4^+$, COF_2^+, ionized in plasma, were measured simultaneously. First, when plasma power increased from 25W to 200W, CF_2^+, $C_2F_4^+$ did not change largely, but CF_2 reduced to one-tenth and C_2F_4 one-hundredth at only 50W. On the other hand, both COF_2^+ and COF_2 did not change largely. Next, when pressure decreased from 2Pa to 0 .5Pa, CF_2^+ kept constant but CF_2 reduced to one-tenth. These results show that behavior of true original molecules is completely different from that of ions ionized in plasma. It is well known too that neutrals such as CF_2, C_2F_4 cannot be detected correctly by electron impact. Therefore it was confirmed that new IAMS is very useful as in-situ monitor in plasma. We would like to present some examples of c-C_4F_8 plasma in manufacturing conditions and of SiH_4 plasma throughout our talk. Precious discussions with Prof. Nakata and Prof. Takayanagi of Tokyo University of Agriculture and Technology are gratefully acknowledged. @FootnoteText@ @footnote 1@ T.Fujii, Mass Spectrometry Review 19(2000) 111, @footnote 2@ M.Nakamura et al, JVST-A 19(2001) 1105,@footnote 3@ Y.Hirano et al, AVS Int.Sympo. PS-TuP3 (2002)

2:20pm **PS-ThA2 Discharge Frequency Dependence of Plasma Parameters in Parallel-plate-electrode VHF Plasmas**, ***Y. Ichikawa,*** Fuji Electric Co. Ltd., Japan; *T. Sasaki,* Fuji Electric CRD, Japan; *S. Matsumura,* Musashi Institute of Technology, Japan

Recently, plasmas generated by power supplies of VHF band attract considerable interest in plasma CVD technique to increase deposition rate and to improve film properties of silicon related thin films. In this work, we have studied the effect of discharge frequency on the characteristics of plasma with a view to understanding the mechanism why VHF plasmas are more desirable than the conventional 13.56MHz plasma. We used a capacitively coupled plasma CVD apparatus with a pair of parallel plate electrodes of 160mm in diameter; the discharge frequency can be varied from 10MHz to 100MHz continuously. To measure the plasma parameters of VHF plasma precisely, we developed the following two probe diagnostic techniques: (1) A modified capacitance probe to measure the amplitude of plasma potential variation (V_{sp-p}) at discharge frequency (2) Compensation single probe by which variation of the plasma potential is compensated and precise current voltage characteristics are measured Employing these probe techniques, we measured electron temperature, electron density, time averaged space potential, and V_{sp-p} in H_2 VHF plasmas. The results measured at frequencies of 13, 24.5 and 92.3MHz show that (1) the electron temperature, Te, decreases with increasing discharge frequency; (2) the electron density for 92.3Hz is about 30 times as high as that for 13MHz under the same discharge power condition. The spatial distributions of these plasma parameters and the space potential were also measured. The details of these experimental results will be presented and discussed.

2:40pm **PS-ThA3 Model-based RF Plasma Monitoring under Industrial Conditions**, ***M. Klick,*** ASI Advanced Semiconductor Instruments, Germany **INVITED**

The increased demand for characterization of plasmas under industrial conditions was mainly driven by the complexity of industrial plasma processes. The interaction of the plasma with the surface determines the quality and performance of the electronic devices on the substrate. Hence a good understanding of the key mechanisms of plasma excitation is required. To address the heating mechanisms of the electrons, knowledge of the electron energy distribution function (EEDF) is imperative - or at least parameters derived from its moments, as the collision rate of electrons for momentum transfer or, taking into account stochastic heating, too, the effective collision rate. Especially the last property, the thermalisation of the electric field's energy, can only be accessed by measuring the self-excited resonance of the electrons in RF plasmas(SEERS, last 's' for spectroscopy). SEERS utilizes nonlinear and resonance effects in the plasma in the sheath and the plasma body leading to a non-sinusoidal RF current. Thus SEERS uses nonlinear and RF effects which usually disturb or even avoid the application of classical methods as Langmuir probes in RF plasmas. The measurement principle is based on a passive RF current sensor and a discharge model involves the effects mentioned above and can be used in reactive plasmas without any restriction. SEERS data based of ten thousands of wafers for different processes show the high efficiency of this approach, in particular under industrial conditions as polymers on chamber wall and sensor itself and undesired effects as arcing at the chamber wall. On the other hand, basic experiments show that plasma physical mechanisms as skin effect in the plasma, ohmic and stochastic heating of electrons can be qualitatively observed in productions tools which are necessary for the understanding and development of process and new chamber types.

3:20pm **PS-ThA5 Study of Pulsed Plasma Doping System by Time-resolved Ion Mass-energy Spectrometry**, ***L. Godet***, *B.-W. Koo,* VSEA, France; *G. Cartry, C. Cardinaud,* Institut des Materiaux de Nantes, France; *Z. Fang,* VSEA, France; *A. Grouillet, D. Lenoble,* STMicroelectronics, France

Pulsed PLAsma Doping (P^2LAD) continues to emerge as a viable alternative technique to ion implantation for advanced semiconductor devices,@footnote 1@ since it is capable of delivering high rate dose at ultra low energy (100V to 10kV applied voltage) giving rise to ultra shallow junctions.@footnote 2@ In P^2LAD, plasma is ignited and extinguished with each negative voltage pulse applied to the wafer. During the pulse, positive ions are accelerated across the sheath and implanted within the wafer. This process was studied using a Hiden EQP mass spectrometer implemented within the pulsed electrode, focussing principally on BF_3 plasma for different implant process conditions. Previous work, employing time averaged mass spectrometry,@footnote 3@ indicated that BF_2^+ is the dominant ion species in the BF_3 plasmas, and BF^+ is the second most abundant ion species. Due to the short (10 - 50µs) pulse length and low repetition rate (100 - 5000Hz) of the P^2LAD process, the time between the pulses is relatively long so that a time-resolved ion mass-energy measurement is necessary to follow the process before, during and after the pulse period. Time resolved Langmuir probe measurements@footnote 4@ have shown the presence of a cold plasma during the afterglow which may be a key parameter for understanding and controlling the entire process (i.e. charge neutralization, etching, deposition). In this paper, we present time-resolved mass spectrometry data allowing a more complete understanding of BF_3 P^2LAD processing including the role of negative charges during the afterglow period. @FootnoteText@@footnote 1@D.Lenoble et al., Ion Implantation Technology 2002, Taos, USA.@Footnote 2@R.B. Liebert et al., Ion Implantation Technology 2000, Alpbach, Austria.@footnote 3@B.W. Koo, Z.Fang, S.Felch, Ion Implantation Technology 2000, Alpbach, Austria@footnote 4@Z.Fang et al., Ion Implantation Technology 2002, Taos, US.

3:40pm **PS-ThA6 Gas-Phase Diagnostics and Mechanisms of Energy Transfer in O_2/NH_3 Plasmas**, ***K.R. Kull***, *D.S. Wavhal, E.R. Fisher,* Colorado State University

Hydrophobic polymeric membranes are used extensively throughout a variety of industrial and biomedical processes. To improve the separation performance, hydrophilic surface modification is required. In this work, we have studied hydrophilic modification of asymmetric porous polyethersulfone membranes using N_2, NH_3 and O_2/NH_3 plasma treatments. Membrane treatments using 100%

N@sub 2@ or 100% NH@sub 3@ plasmas yielded incomplete hydrophilic treatments. In contrast, the O@sub 2@/NH@sub 3@ plasma treatment produced a hydrophilic membrane that retained its hydrophilicity over an extended period after treatment. Examination of the plasma gas-phase composition using optical emission spectroscopy and mass spectrometry revealed the NH radical is present in both the 100% NH@sub 3@ and the O@sub 2@/NH@sub 3@ systems, whereas the OH radical is only observed in the O@sub 2@/NH@sub 3@ plasma. Evidence from other plasma modification systems indicates the OH radical is critical for permanent hydrophilicity using non-polymerizing plasma treatments of polymeric membrane treatments.@footnote 1@ To better understand the chemistry that occurs during these processes, we have used our laser-induced fluorescence based imaging technique to characterize the relative densities of NH and OH and their energy partitioning in these plasmas. The relative densities of both radicals are dependent on the applied rf power (P) and feed gas composition dependent. Interestingly, the rotational temperatures of both species appear nearly independent of P. Surface interactions of NH and OH with membranes, as well as their translational temperatures in the plasma, will be presented and compared to earlier results for NH@sub 2@ radicals in NH@sub 3@ plasma.@footnote 2@ Implications for plasma modification mechanisms will also be discussed. @FootnoteText@@footnote 1@ M. L. Steen, et al., Langmuir 17, 2001, 8156.@footnote 2@ C. I. Butoi, et al.,J. Phys. Chem. B 105, 2001, 5957.

4:00pm **PS-ThA7 The Study of Ion Drift Velocities and Instabilities in Presheaths in Two Ion Species Plasmas***, **X Wang**, E. Ko, N. Hershkowitz,* University of Wisconsin, Madison

The presheath is a region of weak electric field that accelerates ions into the sheath at the plasma boundary. The experiments were performed in multi-dipole DC plasmas with He-Ar gas mixtures (P@sub total@ @>=@ 1.0mTorr, n@sub e@ @>=@ 1x10@super 9@cm@super -3@, T@sub e@ @<=@ 2eV). The concentration of ion species in the two ion species plasmas was determined by measuring ion acoustic wave phase velocity and electron temperature in the bulk region.@footnote 1@ To measure ion drift velocities in the presheath, an ion acoustic wave was launched by both a continuous sinusoidal wave and a pulse, and detected by a cylindrical probe with a boxcar averager. Ion drift velocities were measured in pure Ar plasma. Based on the dispersion relation in the presheath for multi-ion species plasma and phase velocity measurements in He-Ar plasma, the relationship between Ar and He ion drift velocities was determined. Using Ar ion drift velocities from LIF data,@footnote 2@ the He ion drift velocities were determined. In two ion species plasmas, instabilities can be excited by the two ion streams with different drifting velocities that are created in the presheath. Instabilities changing with different partial pressure, positions and discharge current were observed by using a cylindrical probe biased to collect either ion saturation current or electron saturation current and a spectrum analyzer. The frequency of instabilities is ~1.0MHz and wavelength is ~5.0mm compared to ~3.0cm of presheath length. ** Work supported by US DOE grant DE-FG02-97ER54437. @FootnoteText@@footnote 1@A. M. Hala and N. Hershkowitz, Rev. Sci. Instrum. 72, 2279 (2001).@footnote 2@G. D. Severn, Xu Wang, Eunsuk Ko and N. Hershkowitz, Phys. Rev. Lett. 90, 145001 (2003).

4:20pm **PS-ThA8 Ion Collection by a Mach Probe in Flowing Unmagnetized Plasma***, **E. Ko**, X Wang, N. Hershkowitz,* University of Wisconsin, Madison

The measurement of plasma flow along the presheath in unmagnetized plasma is performed using a spherical Mach probe. Ion flow velocity in unmagnetized plasma is examined experimentally and compared to a recent numerical simulation by Hutchinson.@footnote 1@ The spherical Mach probe, which was inspired by Hutchinson's theoretical model, consists of a conducting sphere that has two conducting probe tips, insulated from the sphere and mounted at @theta@ = 0° and 180° with respect to the flow direction. Although the simulation included T@sub i@ = 0.1T@sub e@ ~ 10T@sub e@ and flow velocity v@sub f@ = 0 ~ 3c@sub s@, where c@sub s@ is the sound speed, the laboratory plasma in the presheath was limited to T@sub i@ < 0.1T@sub e@ and v@sub f@ @<=@ 1.0 c@sub s@. The experiment is performed in a multi-dipole DC plasma with Argon pressure ranging from 0.1 to 3mTorr. The upstream and downstream probe tips and the surface of the sphere were simultaneously biased to minimize the probe edge effects, and to obtain a much closer condition to the simulation. This work also examines a previous experiment@footnote 2@ that used the Hudis and Lidsky formula,@footnote 3@ which though shown to be invalid@footnote 4@ still attained results in good agreement with the simulation. *Work Supported by US DOE grant DE-FG02-97ER 54437. @FootnoteText@ @footnote 1@ I. H. Hutchinson, Plasma Phys. Control. Fusion, 44 1953 (2002)@footnote 2@ L. Oksuz, M. A. Khedr, and N. Hershkowitz, Phys. Plasmas, 8 1729 (2001)@footnote 3@ M. Hudis and L. M. Lidsky, J. Appl. Phys., 41 5011 (1970)@footnote 4@ I. H. Hutchinson, Phys. Plasmas, 9 1832 (2002).

4:40pm **PS-ThA9 Novel Plasma Monitoring Scheme by Surface Wave Probe***, **H. Sugai**, H. Kawai,* Nagoya University, Japan*; K. Nakamura,* Chubu University, Japan

A novel and simple technique for measuring the electron density@footnote 1@ and temperature@footnote 2@ of plasma reactors using a surface wave probe (SW probe) is presented. This probe is also called plasma absorption probe as it is based on absorption of surface waves by plasma. The SW probe enables us to measure the local absolute electron density even when the probe surface is soiled with processing plasmas. The technique relies on absorption of surface waves resonantly excited around the probe head at critical frequencies which mainly depend on the electron density. The probe consists of a small antenna connected with a coaxial cable and is enclosed in a tube of dielectric constant @epsilon@@sub d@ inserted in a plasma of electron plasma frequency @omega@@sub p@. A network analyzer feeds a rf signal to the antenna and displays the frequency dependence of the power absorption. The absorption is observed at frequencies slightly above the surface wave resonance frequency, @omega@@sub p@/ (1+ @epsilon@@sub d@),@footnote 1,2@ which allows us to determine the electron density. Use of a pair of SW probes of different sizes enables measurements of both electron temperature and electron density. The measurements were made in a wide range of electron density (10@super 8@ - 10@super 13@ cm@super -3@) and gas pressure (10 mTorr -10 Torr) with high resolutions of space (@DELTA@x~2 mm) and time (@DELTA@t~1 µs). Time-variation of a few percents of electron density is detectable. @FootnoteText@ @footnote 1@H. Kokura, K. Nakamura, I. Ghanashev and H. Sugai, Jpn. J. Appl. Phys. 38, 5262 (1999)@footnote 2@K. Nakamura, M. Ohata and H. Sugai:, J. Vac. Sci. Technol. A21, 325 (2003).

5:00pm **PS-ThA10 Measurement of Absolute Radical and Metastable Species Densities in O@sub 2@ and N@sub 2@ Plasmas using Modulated Beam Appearance Ionization Mass Spectrometry***, S. Agarwal,* University of California, Santa Barbara*; G.W.W. Quax, B. Hoex, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands*; D. Madoudas,* University of Massachusetts, Amherst*; **E.S. Aydil**,* University of California, Santa Barbara

Measurement of radical densities in an electrical gas discharge is important for understanding and improving plasma etching and plasma-assisted deposition processes. We have designed, developed and demonstrated an experimental apparatus for measuring the density of the radicals and electronically excited molecular species in a plasma using modulated beam line-of-sight appearance ionization mass spectrometry (LOS-AIMS). In LOS-AIMS, the species in the plasma are sampled through an aperture on the substrate platen and detected using a quadrupole mass spectrometer (QMS) placed in line-of-sight with this aperture in a three-stage differentially pumped vacuum chamber. Although LOS-AIMS is a versatile tool for measuring absolute radical densities, we show that it requires careful vacuum design and calibration which should take into account various sources of error such as the contribution to the QMS signal from the background gases, the ion mass-to-charge ratio dependence in the sensitivity of the QMS, and space-charge limitations in the QMS ionizer. In addition, collisions within the extracted molecular beam must be taken into account for higher operating pressures in the plasma chamber. Careful consideration of these effects and modulation of the sampled radical beam with a chopper allows the determination of the absolute radical densities, parent molecule concentrations, and the neutral gas temperature near the substrate plane. Specifically, we have measured densities of O and Ar atoms and O@sub 2@ molecules in O@sub 2@/Ar plasma mixtures and N atoms and metastable N@sub 2@ molecules in N@sub 2@ plasmas. In addition, we find that at low pressures, the O@sub 2@ translational temperature is higher than that for Ar. We attribute this difference in Ar and O@sub 2@ translational temperatures to hot O@sub 2@ molecules that are created by O-O recombination reactions on the walls of the plasma chamber which do not equilibrate effectively with Ar atoms at lower pressures.

Biomaterial Interfaces
Room 318/319 - Session BI+PS-FrM
Plasma Methods for Bio-interfaces

Moderator: E.R. Fisher, Colorado State University

8:20am **BI+PS-FrM1 Precision Chemical Control of Plasma Deposition for Smart Biosurfaces*, B.D. Ratner,*** University of Washington **INVITED**

In recent years, methods have evolved to deposit thin organic films from plasma environments that exhibit good control of chemistry along with the uniformity and substrate adhesion expected from plasma deposition. Three examples will be presented illustrating chemical control with special application to biomaterials. (1) Poly(N-isopropyl acrylamide) (pNIPAM) exhibits a solubility transition at 32 Â°C in an aqueous environment. When grafted onto a solid substrate, the pNIPAM phase transition produces a "smart" surface with strongly varying physical properties switchable with small temperature changes. Cells adhere and grow on ppNIPAM at 37Â°C and detach from the surface at room temperature. The ppNIPAM surfaces are non-toxic and excellent for cell growth. A microheater array can spatially control cell attachment to a ppNIPAM-treated chip. This suggests possibilities for cellomic and proteomic devices. (2) Since plasma environments destroy complex biomolecules, a new instrument has been constructed that combines electrospray ionization with plasma treatment of surfaces to produce a fast, efficient, flexible means to treat the surfaces of biomaterials with active biomolecules. The system has been successful in depositing intact, chemically bound hyaluronic acid (HA) onto plasma-activated stainless steel surfaces. (3) Poly(L-lactic acid) (PLLA) has been widely applied in tissue engineering scaffolds or for delivery of bioactive molecules, as it breaks down in the body to lactic acid, a component of the normal metabolism The pulsed plasma deposition techniques has been used to form thin PLLA coatings using cyclic lactide monomer. Such films degrade in a phosphate buffer solution.

9:00am **BI+PS-FrM3 Investigation of Organic Monomers in Plasma-induced Chemical Micropatterning*, G.Sh. Malkov*,** *M.L. Godek, D.W. Grainger, E.R. Fisher,* Colorado State University

Plasma-enhanced chemical vapor deposition (PE-CVD) of organic films is a valuable technique for the surface modifications of polymeric biomaterials. Recently, plasma-based methods have been developed for the fabrication of chemical micropatterns, which have a number of applications, including production of multianalyte biosensors, diagnostic tests, DNA microchips, and genomic arrays. The generation of micropatterns by means of the plasma deposition of organic compounds through a transmission electron microscope (TEM) grid mask has been reported.@footnote 1@ Here, we have created various high fidelity micron-scale patterns of different chemistries using inductively coupled pulsed RF plasma deposition through a TEM grid with the following monomers: acrylic acid, N-vinyl-2-pyrrolidinone, 2-hydroxyethyl methacrylate, N-vinylformamide, allylamine, and hexylamine on PS coated with plasma deposited, highly hydrophobic fluorocarbon materials. SEM images of the patterned surfaces will be demonstrated. Physico-chemical properties of deposited polymeric materials were characterized using angle-resolved XPS, FTIR, spectroscopic ellipsometry, and static contact angle measurements on unpatterned samples, which were plasma treated under identical plasma conditions. Directed cell attachment studies have also been performed. NIH 3T3 fibroblast cells were used to test the cell adhesion and viability on the various patterned surfaces. PS coated with FC is biologically inert: cells do not adhere on this surface. In contrast, cells proliferate well on surfaces functionalized with organic monomers. Other cell culture experiments and biomolecule patterning will be discussed. @FootnoteText@@footnote 1@ N.A. Bullet, R.D.Short et al. Surface and Interface Analysis. 2001, 31, 1074-1076.

9:20am **BI+PS-FrM4 Combining Pulsed RF Plasma Polymer Coatings with Avidin-Biotin Chemistry for On-Probe Affinity Capture Mass Spectrometry*, G.R. Kinsel*,** *M. Li, R.B. Timmons,* University of Texas at Arlington

Matrix assisted laser desorption / ionization mass spectrometry (MALDI-MS) has become a powerful analytical tool for the characterization of proteins. As the effectiveness of the MALDI method has advanced, the need for high-speed isolation and purification of targeted proteins in complex mixtures (e.g. culture media, serum or urine) has increased. The approach described in this presentation focuses on the use of RF plasma polymer coated MALDI probes as platforms for introduction of avidin/biotin chemical modifications. Pulsed RF plasma deposition of allyl amine or vinyl carboxylic acid directly on the MALDI probe surface is used to produce amine modified and carboxylic acid modified surfaces, respectively. Control of the functional group density is achieved through changes in the duty cycle of the pulsed RF plasma. Both amine and carboxylic acid functionalized plasma polymer modified probe surfaces have been investigated as platforms for attachment of avidin or biotin. Testing of the surfaces for peptide/protein isolation based on the targeted properties is performed using various laboratory prepared control mixtures and mixtures obtained from biological sources. In all cases selective capture of the targeted protein/peptide was evaluated through the acquisition MALDI mass spectra using a Bruker BiFLEX linear MALDI TOFMS or a laboratory-constructed linear MALDI TOFMS. Data has been obtained from both avidin and biotin surfaces demonstrating the efficacy of these modified MALDI probe surfaces for achieving on-probe bioselective isolation of target compounds.

9:40am **BI+PS-FrM5 Chemical Modifications of PVC Endotracheal Tubes by RF-Oxygen Glow Discharge Pre-functionalization and NaOH/AgNO@sub 3@ Wet Treatments to Reduce Bacterial Adhesion*, D.J. Balazs,*** *K. Triandafillu,* Swiss Federal Inst. of Tech., Switzerland*; P. Wood,* Univ. Hospital of Geneva, Switzerland*; Y. Chevolot,* Goemar Laboratories, France*; C. van Delden,* Univ. Hospital of Geneva, Switzerland*; H. Harms, C. Hollenstein, H.J. Mathieu,* Swiss Federal Inst. of Tech., Switzerland

The use of silver as an antibacterial agent can be traced back to ancient times, and is currently used in several medical applications.@footnote 1@ Bacterial colonization of intubation tubes is responsible for 90% of all nosocomial pneumonia cases, 40 % of which lead to death, despite aggressive antibiotic therapy.@footnote 2@ We have developed an approach based on the surface modification of medical grade poly(vinyl chloride) (PVC) to create an anti-colonization surface, rich in silver ions. The modification consists of an oxygen plasma treatment, followed by a two step wet treatment in sodium hydroxide (NaOH) and silver nitrate (AgNO@sub 3@) solutions. XPS analysis and contact angle measurements were used to investigate the chemical nature and surface wettability of the films following each step of the modification. Saponification with NaOH of esters, like those of PVC plasticizers was determined to be a simple, irreversible method of hydrolysis, producing sodium carboxylate and phthalate salts. Following a subsequent in incubation in the AgNO@sub 3@ solution, XPS showed evidence of a replacement reaction that produced a surface rich in silver ions. The potential of wet treatments that incorporate silver as a germicidal agent was demonstrated in bacterial and biofilm studies, using various P. aeruginosa strains. The native and O@sub 2@ pre-functionalized PVC surfaces submitted to the wet treatments exhibited a 100% reduction in initial bacterial adhesion. The efficacy of the wet treatment to reduce colonization over a longer period was demonstrated as 7-logarithmic drop in biofilm population at 24h and an 8-logarithmic reduction at 72 h, as compared to native PVC substrates. @FootnoteText@@footnote 1@ R.O. Darouiche, (1999) Clin. Infect. Dis. 29, 1371-1377. @footnote 2@ J.L. Vincent, D.J. Bihari, et al., (1995) JAMA 274: 639-644. .

10:00am **BI+PS-FrM6 PECVD Growth and Ion Beam Modification of Polymer Films with Patterned Surface Charge Properties*, A. Valsesia*,** *M. Manso, G. Ceccone, D. Gilliland, F. Rossi,* Joint Research Centre, Ispra, Italy

The performance of polymer films in biomedical devices such as DNA arrays and other biosensors depends greatly on the ability to control their surface properties. In fact, surface features determine the ability of the polymer to immobilize a target biomolecule or to give this molecule an orientation towards adsorption. Plasma enhanced chemical vapor deposition (PECVD) of Polymers is an attractive way to produce this kind of films due to the high rate of functional groups obtained at energies ensuring film stability. The density of functional groups can be modified by an Ion Beam Modification. If this last treatment is performed through a mask, the surface remains with regions expressing different responses to chemical groups and environmental free charges (i.e. ions in solution). In this work we have studied the properties of two polymers with contrasted surface charge behavior. Allylamine (AlA) and Acrylic Acid (AcA) films were studied in parallel by Fourier transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) outlining the changes occurred during plasma polymerization and ion beam modification. These spectroscopic results were correlated with wetting and surface charge behavior by performing contact angle and Z-potential measurements. Their stability and ability for protein adsorption was evaluated by using a quartz crystal microbalance (QCM-D). The possible interference with topographic features has been tested by observing the films in an atomic force

microscope, which was further used to monitor electric fields in buffer solutions. From these results we conclude that the combination of PECVD and ion beam modification is an effective way for the growth of polymer films with controlled properties for bio-sensing applications.

10:20am **BI+PS-FrM7 Growth of Biodegradable Thin Films by Methods of Pulsed Laser Deposition***, **J.M. Fitz-Gerald**, A.L. Mercado, L. Zhigilei, R. Johnson, C.L. Fraser,* University of Virginia*; J.D. Talton,* Nanotherapeutics, Inc.

Poly(DL-lactide-co-glycolide) (PLGA) is a biodegradable polymer with application in many areas of biomedical field ranging from contact lenses to sustained drug release formulation. In this research thin films (25 nm - 5 microns) of PLGA were deposited onto Si and NaCl wafers, in addition, a specific class of particulate materials (inhaled steroids) ranging from 1-5 microns in size were coated for in-vitro testing. All coatings were processed by both conventional pulsed laser deposition (PLD) and matrix-assisted pulsed laser evaporation (MAPLE) techniques. Film morphology, chemical structure, and decomposition effects were characterized by scanning electron microscopy (SEM), Fourier transform infrared infrared spectroscopy (FTIR), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and in-vitro dissolution.

10:40am **BI+PS-FrM8 Study of RGD Peptide and Fibronectin Adsorption on Polymer Surfaces Micropatterned by Cold Plasma and Ion Beams***, **C. Satriano**,* University of Catania, Italy*; M. Manso,* Joint Research Centre, Ispra, Italy*; N. Giamblanco,* University of Catania, Italy*; G. Ceccone, D. Gilliland, F. Rossi,* Joint Research Centre, Ispra, Italy*; G. Marletta,* University of Catania, Italy

Thin films of polycaprolactone (PCL) and polyhydroxymethylsiloxane (PHMS) were patterned by Ar@super +@ ions beams or cold microwave Ar plasmas through Ni masks. The dimensions of the patterns stripes and pitches were typically between 30 and 100 µm. In the case of Ar@super +@ irradiation, the two ion energies of 50 keV and 0.5 keV were used, with fluences ranging from 1x1014 to 5x1015 ions/cm@super 2@. For plasma irradiation, the samples were placed on a grounded or RF biased sample holder (-50V), for different times. The surface structure and composition changes were characterized by spatially resolved X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface roughness on the micro- and nanometer scale was determined by Atomic Force Microscopy (AFM). The surface charge and dispersive/polar forces distribution were determined by Zeta Potential (ZP) and Surface Free Energy (SFE) measurements respectively. Finally the change of thickness and visco-elastic properties of the films was investigated by the Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) technique. The adsorption of RGD peptide sequences and fibronectin was investigated as a function of the different treatment parameters, including ion energy and dose. The in-situ kinetics of adsorption and modeling of the viscoelastic properties of the adsorbed layers were studied by using QCM-D technique, while the chemical structure and lateral distribution of the adlayers were characterized ex situ by Small Spot XPS, ToF-SIMS Imaging measurements and AFM. The results showed that selective patterning of the adsorbed peptide and fibronectin could be achieved mainly in connection with the polar to dispersive ratio of the surface free energy. In particular, the surface modification seems to affect also the morphology adlayers.

11:00am **BI+PS-FrM9 Chemical Modification of a Three-dimensional Tissue Engineering Polymeric Scaffold by Low-temperature Radio-frequency Plasma Treatment***, **S. Kumar**,* University of South Australia, Australia*; R.St.C. Smart,* University of South Australia*; D.J. Simpson,* University of South Australia and Seoul National University, Korea

The technique of low-temperature radio-frequency plasma has been employed for the chemical modification of Osteofoam, a three-dimensional polymeric (PLGA) tissue engineering scaffold material. The chemical modification in question was aimed at coating Osteofoam with a thin layer of silica, both on its surface as well as in its bulk. For this, Osteofoam cubes of dimensions 12 mm x 12 mm x 12 mm were treated with the plasma generated using tetraethoxysilane (TEOS) as the main precursor. The chemical modification thus achieved was investigated and quantified using the X-ray photoelectron spectroscopy technique, revealing the presence of silica both on the surface as well as in the bulk of Osteofoam samples. The XPS data also suggest that the plasma process developed and employed by us is relativley more efficient at modifying the sample surface than its bulk.

11:20am **BI+PS-FrM10 Deposition of Amine Containing Films from Hyperthermal Silazane and Allyl Amine Ions***, A. Choukourov, H. Biederman,* Charles University, Czech Republic*; E. Fuoco, S. Tepavcevic, **L. Hanley**,* University of Illinois at Chicago

Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces. We have previously shown that fluorocarbon and siloxane ions can be employed for the growth and modification of organic thin films on polymer, semiconductor, and metal surfaces.@footnote 1-3@ These films are often similar in chemical composition to plasma polymers, due at least in part the presence of large, hyperthermal positive ions in many plasmas. This work deposits beams of mass-selected 5 - 200 eV silazane and allyl amine ions onto aluminum and silicon substrates. Silazane and allyl amine ions are produced by electron impact ionization of 1,3-divinyltetramethyldisilazane and allyl amine, respectively. These ion-deposited films are analyzed by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy. Chemical functionalization prior to XPS analysis permits the unique identification of primary and secondary amine groups. Secondary amine containing films are shown to form at low silazane ion energies whereas the higher ion energies lead to formation of more inorganic, silico-carbo-nitride-like films. Primary amines are produced by allyl amine ions at various energies. Films grown by allyl amine ion deposition are compared with those produced by plasma polymerization of allyl amine. Effects of film aging in air are also discussed. @FootnoteText@ @footnote 1@L. Hanley and S.B. Sinnott, Surf. Sci. 500, 500 (2002). @footnote 2@P.N. Brookes, S. Fraser, R.D. Short, L. Hanley, E. Fuoco, A. Roberts, and S. Hutton, J. Elec. Spect. Rel. Phenom. 121, 281 (2001).@footnote 3@E.R. Fuoco and L. Hanley, J. Appl. Phys. 92, 37 (2002).

11:40am **BI+PS-FrM11 Plasma Chemistry of Allylamine for the Deposition of Nitrogen-Containing Organic Films***, **D.C. Guerin**,* Naval Research Laboratory, National Research Council*; V.A. Shamamian, R.T. Holm,* Naval Research Laboratory

We studied the chemistry of an allylamine/argon plasma for the deposition of nitrogen-containing organic films. We used in situ mass spectrometry to determine the identity of the molecular ion flux to the deposition surface. Our investigation showed that under the span of powers interrogated (30-100 W) the identity of the ion flux did not substantially change. The total ion current to the deposition surface increased linearly with plasma power. However, the molecular ion mass distribution changed with the plasma pressure. In lower-pressure plasmas, the predominant ions were generated by electron-impact ionization reactions. At higher pressures ions generated by ion-molecule reactions dominate the flux to the surface. We used appearance potential mass spectrometry to confirm the creation of NH@sub 3@ as a by-product of the ion-molecule reactions. The resulting films were characterized optically. The deposition rates were highly dependent on the plasma power. However, the indicies of refraction were similar for the conditions studied. Infrared spectroscopy of the films showed that different plasma conditions resulted in only small changes in film structure. We determined that the film deposition mechanism was not controlled by plasma-ion chemistry. This contrasted with earlier results involving a saturated monomer. However, the film structure was highly dependent on the film thickness. The N-H signal increased greatly in the thicker films. Fluorescamine tagging of the amine groups in the films showed that the primary amine concentration was not well correlated to the intensity of the N-H stretch in the infrared spectra.

Plasma Science and Technology
Room 315 - Session PS-FrM

Plasma-Surface Interactions: Etching

Moderator: H. Blom, Uppsala University, Sweden

8:20am **PS-FrM1 Multidimensional Plasma Sheaths and Resulting Ion/Fast Neutral Distributions on the Substrate Surface***, **D.J. Economou**, D. Kim,* University of Houston

Multidimensional plasma sheaths are encountered in diverse processes including plasma immersion ion implantation, extraction of ions (or plasma) through grids, MEMS fabrication, neutral beam sources, and plasma contact with internal reactor parts (e.g., wafer chuck edge). The sheath may become multidimensional when: (a) plasma is in contact with surface topography, and the size of the topographical features is comparable to the plasma sheath thickness, or (b) the surface is flat but inhomogeneous, i.e., a conducting surface next to an insulating surface. In either case, the flux,

energy and angular distributions of energetic species incident on the substrate are of primary importance. These quantities depend critically on the shape of the meniscus (plasma-sheath boundary) formed over the surface. A two-dimensional fluid/Monte Carlo simulation model was developed to study multidimensional sheaths. 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 a surface with a trench will be reported in detail and compared with experimental data. Results for a flat but inhomogeneous surface will also be reported. @FootnoteText@ Work supported by the National Institute of Standards and Technology, National Science Foundation and Sandia National Laboratories.

8:40am **PS-FrM2 Study of Gas Phase Fluorocarbon Chemistries in a Modified Gaseous Electronics Conference Plasma Reactor Using Fourier Transform Infrared Spectroscopy and Ellipsometry*, B. Zhou,*** *E.A. Joseph, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas at Dallas

Fluorocarbon chemistries of CF@sub 4@ plasmas during dry etching are studied in the modified Gaseous Electronics Conference (mGEC) Reference cell, using Fourier Transform Infrared (FTIR) spectroscopy. These measurements are enhanced by the use of a multi-pass White cell with capabilities up to 40 passes. The flexible design of the mGEC reactor allows us to study the effect of the dimensions, materials and wall conditions of a plasma reactor on the gas phase and surface phase chemistries, as well as the interactions between them. Three sets of inner walls with diameters of 20.3, 40.6, and 61 cm are used and the wall temperature can be raised above 100°C. The gap between the quartz window and chuck can be varied from 2.7cm to 18 cm. For a 5 cm gap, the IR spectra show that the concentrations of CF@sub 2@ and CF@sub 3@ radicals and etch products such as SiF@sub 4@ and COF@sub 2@, are strongly dependent upon the bias voltage. The concentration of CF@sub 2@ radicals is raised by about an order of magnitude to 10@sup 13@ cm@sup -3@ when the chuck self-bias voltage is changed from 0 to -40V. In addition, the concentration ratio of CF@sub 2@ to CF@sub 3@ increases as the bias voltage is made more negative due to an increased etch rate and increased consumption of F atoms. These gas phase measurements will also be compared with etch rate measurements using in-situ spectroscopic ellipsometry. Finally, the experimental data will be compared with simulation results using HPEM.@footnote 1@ This work is supported by a grant from NSF/DOE, CTS-0078669. @FootnoteText@ @footnote 1@ D. Zhang and M. J. Kushner, "Surface Kinetics and Plasma Equipment Model for Si Etching by Fluorocarbon Plasmas", J. Appl. Phys. 87, 1060 (2000).

9:00am **PS-FrM3 Measurement and Modeling of Plasma Feature Etching*, H.H. Sawin*[1]*,*** Massachusetts Institute of Technology **INVITED**

This paper reviews the progress in the understanding of plasma surface interactions. The understanding of the surface kinetics of plasma surface interactions is critical in the efficient development of plasma processes. Our fundamental understanding of plasma-surface interactions has in large part been based on beam experiments in which the flux from a plasma process is synthesized by a combination of beams. The use of beams rather than a plasma source allows the independent control of the beam fluxes. The measurement of polysilicon etching in fluorine and chlorine plasmas has been particularly successful because of its relatively simple discharge chemistry; however, the inclusion of product and polymer deposition during the etching process has typically not been included in kinetic models. The etching of dielectric materials with fluorocarbon gases is much more complex because of the large number of ions and neutral species that must be considered. The use of beams generated from complex plasmas that produce multiple products can be used to better represent the fluxes; however, these studies sacrifice some independence in the control of the fluxes. Based on the kinetic measurements and kinetic models developed from the beam studies, feature profile evolution has been modeled using several approaches, especially Monte Carlo techniques that allow the inclusion of all known kinetics. Deposition processes in which the surface is covered with a material of a single composition is particularly easy as the surface chemistry is does not vary with time or feature position. In etching processes, the surface kinetics are known to be a function of the composition of the feature position and is more complicated since the surface composition varies. In addition, for the deposition of "polymer film" onto the surface during etching to be included for direction etching processes, the polymer film thickness and composition must be tracked as the simulation proceeds.

9:40am **PS-FrM5 The Influence of Ion Implantation on the Poisoning Mechanism During Reactive Magnetron Sputtering*, D. Depla,*** *R. De Gryse,* University Ghent, Belgium

During reactive sputter deposition, the interaction of the plasma with the target surface strongly influences the deposition process and the deposited layer characteristics. Besides chemisorption of the active species on the target surface, reactive ions become implanted in the target subsurface region. An analytical model is proposed describing the effect of ion implantation on the poisoning mechanism during reactive magnetron sputtering. We assume that the target can be described by a mixture of the original target material and the compound material formed by reactive ion implantation. The target is subdivided into three regions :i) the surface region, ii) the subsurface region and iii) the bulk region. The sputter removal of the compound material from the target surface region is balanced by the compound formation by reactive ion implantation in the subsurface and bulk region. The steady-state solution shows a small but abrupt change of the deposition rate. The abrupt change in deposition rate is accompanied by a much larger abrupt change of the target condition in the subsurface region. Moreover, a narrow hysteresis region is found. Several experimental results can be easily explained from this analytical model. As this analytical approach neglects several aspects of the sputtering process, e.g. knock-on effects, recoil mixing, range shortening, we have also simulated this process using TRIDYN. More specific, the influence of reactive ion implantation during the reactive sputtering of Al in Ar/O2 is simulated.@footnote 1@ The results of these simulations confirm not only the basic ideas described by the analytical model, but a quite good agreement between both models is found. @FootnoteText@ @footnote 1@Z.Y. Chen, A. Bogaerts, D. Depla, I. Ignatova, Nucl. Instr. And Meth. B, accepted for publication.

10:00am **PS-FrM6 The Role of Chamber Dimension in Fluorocarbon Etching of SiO@sub 2@ and its Effects on Gas and Surface-Phase Chemistry*, E.A. Joseph,*** *B. Zhou, S.P. Sant, L.J. Overzet, M.J. Goeckner,* University of Texas - Dallas*; B.E. Gnade,* University of North Texas

The influence of plasma-wall interactions in a CF4 discharge and their symbiotic effect on processing of SiO2 has been explored as a function of chamber dimension using a modified gaseous electronics conference (mGEC) reference cell. By varying chamber wall diameter, 20-66 cm, and source-platen distance, 4 - 6 cm, the etch behavior of SiO2 and the resulting gas-phase chemistry change significantly. Results from in-situ spectroscopic ellipsometry show significant differences in etch characteristics, with etch rates as high as 700nm/min and as low as 150nm/min for the same self-bias voltage. Etch yields however remain unaffected by the chamber size variations. Fluorocarbon deposition rates are also highly dependent on chamber dimension and vary from no net deposition to deposition rates as high as 450 nm/min. Significant shifts in gas-phase properties such as electron density and electron temperature, as determined by Langmuir probe, are also measured while gas-phase in-situ multi-pass Fourier Transform Infra-Red spectroscopy (FTIR) is used to corrleate CF2, CF3 and CF4 gas-phase densities to CFx overlayer thickness and stoichiometry measured by x-ray photoelectron spectroscopy (XPS) and grazing angle total internal reflection (GATIR-FTIR). @FootnoteText@ This work is supported by a grant from NSF / DOE, CTS-0078669.

10:20am **PS-FrM7 Molecular Dynamics Simulations of Silicon in Fluorocarbon Plasmas: Role of the Fluorocarbon Film as an Etchant Source*, D. Humbird,*** *D.B. Graves,* University of California at Berkeley*; X. Hua, G.S. Oehrlein,* University of Maryland, College Park

We use MD simulations to examine fluorocarbon (FC) ions and radicals impacting Si and compare these simulations to new experimental results. During FC plasma etching of Si, Oehrlein and coworkers observe changes in surface chemistry as ion energy is increased above the threshold necessary for etching, and/or when a large fraction of the impinging ions are Ar@super +@. The F/C ratio of the film decreases and Si-C, C-C, and Si-F bonds all increase in number with the onset of etching. These results were interpreted to mean that F is driven from the FC film into the underlying Si, creating etch products. In simulations of Si etching with CF@sub x@@super +@ species with and without Ar@super +@, we observe a change in the composition of the FC film as the ion energy increases from a depositing to an etching level. The FC film formed at lower energy is comprised almost entirely of C-F@sub x@ groups. At higher energy (>50 eV), Si etching commences, C-F@sub x@ groups are greatly reduced, and

[1] **AVS 50th Anniversary Invited Speaker**

SiF_x bonds form. The FC film becomes stratified, with Si-C at the surface of the film, and Si-F (the etch precursor) underneath. These results are in excellent agreement with XPS measurements of Si samples etched by FC plasmas. Oehrlein and co-workers concluded from their measurements that the FC film contains the etchant F. The simulations confirm that F can reach the Si by way of the FC film. We identify the mechanisms for ion-induced redistribution of F between the FC film and substrate.

10:40am **PS-FrM8 Surface Kinetics Study of Silicon Oxide Etching with Fluorocarbons Plasmas***, **O Kwon**, H.H. Sawin,* Massachusetts Institute of Technology

Fluorocarbon plasma for silicon oxide etching is a complicated system involving many ion and neutral species. Depending on the plasma condition, many difficulties arise such as RIE lag, etch stop, and low selectivity to photoresist. For a better understanding of the process it is necessary to have an appropriate physical model to describe the surface kinetics including simultaneous etching and deposition. We developed a surface kinetic model using ABACUSS II, a modeling environment and simulator. In the modeling we included the effect of both neutral and ion fluxes to the surface, sticking probabilities, surface composition, sputter etching reactions, ion enhanced chemical etching reactions and neutral-to-ion flux ratio. We demonstrated this model by applying it to various systems such as silicon etching with chlorine/fluorine plasma, silicon oxide etching with chlorine/fluorine plasma and silicon oxide etching with fluorocarbon plasma. This model was verified using measured etching yield data determined by quartz crystal microbalance (QCM) in conjunction with plasma neutral and ion concentrations/fluxes determined by mass spectrometry.

11:00am **PS-FrM9 Integrated Modeling of Etching, Cleaning and Barrier Coating PVD for Porous and Conventional SiO_2 for Fluorocarbon Based Chemistries[1]***, **A. Sankaran**, M.J. Kushner,* University of Illinois at Urbana-Champaign

The modeling of process integration of advanced materials for interconnect wiring can provide insights to methods to optimize the process. This is particularly true for nontraditional materials, such as porous silica. In this work we discuss the modeling of the process integration steps of etch, clean and barrier coating for porous SiO_2 using a feature profile simulator coupled to a plasma equipment model. Results will be discussed for ICP and MERIE reactors for etching of conventional and porous SiO_2 for C_2F_6, CHF_3 and C_4F_8 in mixtures with Ar and O_2. The etch step is followed by the stripping of the residual fluorocarbon polymer layer and of the photoresist. The cleaned features then receive a barrier coating by IMPVD. Etch rates and profiles for interconnected and closed pore networks will be presented. In general, larger molecular weight fluorocarbon gases produce more polymerizing fluxes to the substrate leading to thicker polymer films and hence slower etch rates. Polymer build-up due to opening of large pores and interconnected pore networks leads to slower etching. Increasing O_2 during the etch step reduces polymer buildup but also erodes the photoresist, resulting in less taper (possibly bowing) due to the broader view angles of the incident ion fluxes. Removal of polymer from the pores during the clean step, particularly when interconnected, is problematic. Conformal metal films (for the barrier layer) on porous substrates are more difficult to achieve for larger pores and higher interconnectivities due to shadowing of ion fluxes caused by the complex pore morphology.

[1] Work supported by Semiconductor Research Corporation SEMATECH and National Science Foundation.

11:20am **PS-FrM10 Analysis of ILD Sidewall Damage during Photoresist Removal Post Single and Dual Damascene Processing***, **N.C.M. Fuller**, T.J. Dalton, M.E. Colburn, S.M. Gates,* IBM T.J. Watson Research Center*; R. Dellaguardia,* IBM Microelectronics Division

The introduction of CVD and SOD low-κ organosilicate (OSGs) materials for 90 nm and beyond CMOS back end of the line (BEOL) technologies presents several process challenges. One such challenge is the minimization of ILD sidewall damage during photoresist removal post single and dual damascene processing. The determination of the composition, thickness, and probable mechanism of formation of the damaged layer is critical to its control, prevention, and/or removal and, thus, device performance, functionality, and reliability. To these ends, experimental measurements including XPS and TEM/EELS were performed to characterize the damaged layer formed on an OSG and a porous OSG material exposed to various strip chemistries in a commercial plasma etching tool. These results will be presented.

Author Index

Bold page numbers indicate presenter

— A —
Abe, J.: PS-TuA5, 10
Adamson, S.: PS-TuA7, 10
Agarwal, S.: PS1-WeA8, 22; PS-ThA10, 30
Alami, J.: PS-MoA1, **5**
Albrecht, R.M.: PS2-WeA7, 23
Aldea, E.: PS2-WeA3, **23**
Allen, S.D.: PS-TuA3, 10
Amano, H.: PS-TuP11, 13
Anderle, M.: PS1-WeM7, 16
Ando, A.: PS2-ThM5, 27
Ando, Y.: PS-TuP11, 13
Angelopoulos, M.: PS-TuA3, 10
Annapragada, R.: PS-TuM7, 9
Arefi-Khonsari, F.: PS1-ThM3, **25**
Arikado, T.: PS-MoM9, 2
Asmussen, J.: PS2-WeA6, 23; PS-WeP16, 20
Austin, D.W.: PS1-WeM4, 15
Aydil, E.S.: PS+MM-MoA5, 3; PS+MM-MoA6, 3; PS1-WeA8, 22; PS-ThA10, **30**
— B —
Babayan, S.E.: PS2-WeA2, 22; PS-MoA7, 5
Badowski, P.R.: PS-TuM8, 9
Baek, K.H.: PS1-WeM8, 16; PS-TuP2, **12**
Bai, K.H.: PS-MoM4, **1**
Baker, C.: PS1-WeM3, **15**
Balazs, D.J.: BI+PS-FrM5, **31**
Barnat, E.V.: PS-TuM2, **8**
Barrell, Y.: PS1-ThM7, 25
Barrett, D.: PS+MM-MoA1, 3
Basillais, A.: PS+MM-MoA7, 4; PS-WeP3, 18
Bathke, R.D.: PS2-WeA7, 23
Bayiati, P.: PS1-ThM2, 25
Beijerinck, H.C.W.: PS-MoM7, 1
Belen, J.: PS+MM-MoA5, **3**; PS+MM-MoA6, 3
Benck, E.C.: PS-TuM8, 9; PS-TuP13, **14**
Benedikt, J.: PS+TF-TuM4, **7**
Biederman, H.: BI+PS-FrM10, 32
Blackwell, D.D.: PS1-WeA3, 21; PS-MoA9, 6; PS-WeP10, 19
Blain, M.G.: PS+MM-MoA10, 4
Bloomfield, M.O.: PS2-ThM6, 27
Blumenthal, R.: PS2-WeM7, 17
Bogart, K.H.A.: PS-TuP7, 13
Borges, C.: PS-MoA2, 5
Bose, D.: PS-MoA8, **6**
Boudouvis, A.G.: PS+MM-MoA8, 4
Boufnichel, M.: PS+MM-MoA7, 4
Boukouras, C.: PS+MM-MoA8, 4
Briber, R.M.: PS1-WeM7, 16
Briggs, R.D.: PS-TuP7, 13
Brinker, C.J.: PS2-ThM8, 27
Brueck, S.R.J.: PS2-ThM8, 27
Burke, E.: PS2-ThM10, 28
— C —
Cachet, H.: PS1-ThM3, 25
Cale, T.S.: PS2-ThM6, 27
Campo, M.: PS-MoA2, 5
Cardinaud, C.: PS2-ThM3, 26; PS-ThA5, 29
Carter, C.B.: PS1-WeM2, 15
Cartry, G.: PS2-ThM3, 26; PS-ThA5, 29
Caughman, J.B.O.: PS1-WeM4, **15**
Cecchi, J.L.: PS-TuM9, 9
Ceccone, G.: BI+PS-FrM6, 31; BI+PS-FrM8, 32
Celii, F.G.: PS2-ThM11, 28
Ceylan, A.: PS1-WeM3, 15
Chan, L.: PS-MoM8, 2
Chan, S.H.D.: PS2-WeM4, 17
Chang, C.H.: PS-WeP1, 18; PS-WeP11, **19**
Chang, J.P.: PS+MM-MoA10, 4; PS2-WeM3, 16
Chen, F.F.: PS-MoA5, **5**
Chen, J.: PS2-WeM4, **17**
Chevolleau, T.: PS2-ThM7, 27
Chevolot, Y.: BI+PS-FrM5, 31
Chi, K.K.: PS-MoM4, 1
Cho, B.U.: PS-WeP4, 18
Choukourov, A.: BI+PS-FrM10, 32
Chrpbak, C.: PS+TF-TuM11, 8
Chung, K.H.: PS-TuP14, 14
Coburn, J.: PS1-WeA10, 22
Coghe, N.: PS1-WeM7, 16
Colburn, M.E.: PS-FrM10, 34
Cooperberg, D.J.: PS+MM-MoA5, 3; PS-MoM10, **2**
Cross, K.C.: PS-TuP7, **13**
Cruz, D.: PS+MM-MoA10, **4**
Cunge, G.: PS-TuM5, 8
— D —
Dalton, T.J.: PS+MM-MoA1, 3; PS1-WeM1, 15; PS-FrM10, 34; PS-TuA1, **10**
De Gryse, R.: PS-FrM5, 33
Dellaguardia, R.: PS-FrM10, 34
Dementev, A.: PS-TuA7, 10
Depla, D.: PS-FrM5, **33**
Dheandhanoo, S.: PS-TuM8, 9
Donnelly, V.M.: PS-TuM3, **8**
Druz, B.: PS-MoA2, 5
Dussart, R.: PS+MM-MoA7, 4; PS-WeP3, 18
— E —
Economou, D.J.: PS-FrM1, **32**; PS-WeP12, 19
Efremov, A.M.: PS-TuP8, 13; PS-WeP6, **18**
Egami, A.: PS1-WeA4, 21
Endo, K.: PS2-WeA4, 23
Eon, D.: PS2-ThM3, **26**
Esnault, S.: PS2-WeA7, 23
— F —
Fang, Z.: PS-ThA5, 29
Fernsler, R.F.: PS1-WeA3, 21; PS-MoA9, 6; PS-WeP10, 19
Fisher, E.R.: BI+PS-FrM3, 31; PS1-ThM8, 26; PS1-WeA6, 21; PS-ThA6, 29
Fitz-Gerald, J.M.: BI+PS-FrM7, **32**
Fraser, C.L.: BI+PS-FrM7, 32
Fraser, D.: PS1-WeA10, 22
Fujii, T.: PS-ThA1, 29
Fuller, N.C.M.: PS-FrM10, **34**
Fuoco, E.: BI+PS-FrM10, 32
— G —
Garwood, G.A.: PS2-WeM8, 17
Gates, S.M.: PS-FrM10, 34
Gerberich, W.W.: PS1-WeM2, 15
Gerung, H.: PS2-ThM8, **27**
Giamblanco, N.: BI+PS-FrM8, 32
Gianchandani, Y.: PS+MM-MoA3, **3**
Gidwani, A.: PS1-WeM2, 15
Gilliland, D.: BI+PS-FrM6, 31; BI+PS-FrM8, 32
Gillis, H.P.: PS2-WeM8, 17
Girshick, S.: PS1-WeM2, 15
Gnade, B.E.: PS-FrM6, 33
Godek, M.L.: BI+PS-FrM3, 31
Godet, L.: PS-ThA5, **29**
Goeckner, M.J.: PS-FrM2, 33; PS-FrM6, 33; PS-TuM11, 9
Gogolides, E.: PS+MM-MoA8, 4; PS1-ThM2, 25
Goldfarb, D.: PS-TuA3, 10
Gomez, S.: PS+MM-MoA5, 3; PS+MM-MoA6, **3**
Gong, M.L.: PS-WeP11, 19
Goorsky, M.S.: PS2-WeM8, 17
Goto, T.: PS-TuP1, 12
Goto, T.K.: PS-TuM10, 9
Gottscho, R.A.: PS-MoM1, **1**
Govindan, T.R.: PS-MoA8, 6
Grainger, D.W.: BI+PS-FrM3, 31
Graves, D.B.: PS1-WeA10, 22; PS-FrM7, 33
Grotjohn, T.A.: PS2-WeA6, **23**; PS-WeP16, 20
Grouillet, A.: PS-ThA5, 29
Gudmundsson, J.T.: PS-MoA1, 5
Guerin, D.C.: BI+PS-FrM11, **32**
Guillorn, M.A.: PS1-WeM4, 15
Gylfason, K.B.: PS-MoA1, 5
— H —
Hafiz, J.: PS1-WeM2, 15
Hamaguchi, S.: PS1-ThM11, 26
Han, S.M.: PS2-ThM8, 27
Han, W.S.: PS-MoM4, 1
Hane, K.: PS+MM-MoA9, 4
Hanley, L.: BI+PS-FrM10, **32**
Hanyu, I.: PS-MoM6, 1
Harms, H.: BI+PS-FrM5, 31
Hata, D.M.: PS-WeP17, **20**
Hayashi, H.: PS-TuA5, **10**
Hayes, A.V.: PS-MoA2, **5**
Heberlein, J.V.R.: PS1-WeM2, 15
Hebner, G.A.: PS-TuM1, **8**; PS-TuM2, 8
Heckscher, M.: PS2-ThM9, 28
Helmersson, U.: PS-MoA1, 5
Hemawan, K.: PS2-WeA6, 23
Hershkowitz, N.: PS-ThA7, 30; PS-ThA8, 30
Hess, D.W.: PS-TuM8, 9
Hicks, R.F.: PS2-WeA2, 22; PS-MoA7, 5
Hiramatsu, M.: PS-TuP11, 13
Hirano, Y.: PS-ThA1, 29
Hoefnagels, J.P.M.: PS1-ThM7, **25**
Hoex, B.: PS-ThA10, 30
Hollenstein, C.: BI+PS-FrM5, 31
Holm, R.T.: BI+PS-FrM11, 32
Hong, J.: PS1-ThM10, 26
Horak, D.: PS-MoM10, 2
Hori, M.: PS2-ThM1, **26**; PS-TuP1, 12; PS-TuP11, 13
Horikawa, T.: PS2-WeM1, 16
Hua, X.: PS1-ThM9, 26; PS1-WeM7, **16**; PS2-ThM11, 28; PS-FrM7, 33
Hudson, E.A.: PS1-ThM9, 26; PS-TuM7, **9**
Humbird, D.: PS-FrM7, **33**
Hussein, M.: PS2-ThM9, **28**
— I —
Ichikawa, Y.: PS-ThA2, **29**
Ichiki, K.: PS-MoM9, 2
Ida, T.: PS-MoM9, 2
Im, Y.H.: PS2-ThM6, **27**
Inoue, N.: PS2-ThM4, 27
Ishii, N.: PS-TuP10, 13
Ishikawa, K.: PS1-WeA9, 22
Ishikawa, Y.: PS1-WeA5, **21**
Itagaki, N.: PS-TuP10, **13**
Ito, M.: PS-TuP1, **12**
Iwawaki, M.: PS-TuP1, 12
Izawa, M.: PS-MoA10, 6
— J —
Jang, K.H.: PS-TuP3, **12**
Ji, B.: PS-TuM8, **9**
Jiang, P.: PS2-ThM10, **28**; PS2-ThM11, 28
Jin, W.: PS-MoM5, **1**
Jindal, A.K.: PS-TuM11, **9**
Johnson, R.: BI+PS-FrM7, 32
Johnson, S.M.: PS2-WeM8, 17
Johnston, S.: PS-MoM10, 2
Jolly, T.W.: PS-MoA3, 5
Joseph, E.A.: PS-FrM2, 33; PS-FrM6, **33**
Joubert, O.: PS2-ThM7, 27; PS-MoM3, 1; PS-TuM5, 8
Jung, S.J.: PS1-WeM8, 16; PS-TuP2, 12
Jurczyk, B.: PS+TF-TuM11, **8**
— K —
Kadoya, T.: PS-TuP11, 13
Kaguchi, N.: PS1-WeM6, 15
Kanarov, V.: PS-MoA2, 5

Author Index

Kang, C.J.: PS1-WeM8, 16; PS-MoM4, 1; PS-TuP2, 12
Karahashi, K.: PS1-WeA9, 22; PS2-WeM1, **16**
Karwacki, E.J.: PS-TuM8, 9
Kawai, H.: PS-ThA9, 30
Kawai, Y.: PS-TuP10, 13
Keil, D.: PS-TuM7, 9
Kessels, W.M.M.: PS1-ThM10, 26; PS1-ThM7, 25
Kiehlbauch, M.W.: PS+MM-MoA5, 3; PS+MM-MoA6, 3
Kim, C.I.: PS-TuP4, 12; PS-TuP5, 12; PS-TuP6, 13; PS-TuP8, 13; PS-WeP6, 18
Kim, C.-K.: PS+MM-MoA2, 3
Kim, D.: PS-FrM1, 32
Kim, D.P.: PS-TuP4, 12; PS-TuP5, 12; PS-TuP6, 13; PS-TuP8, **13**; PS-WeP6, 18
Kim, H.R.: PS-TuP3, 12
Kim, J.: PS2-WeM8, **17**
Kim, J.H.: PS-TuP14, **14**
Kim, J.K.: PS-TuP4, **12**
Kim, K.N.: PS-WeP4, **18**
Kim, K.T.: PS-TuP4, 12; PS-TuP5, 12; PS-TuP6, 13; PS-TuP8, 13
Kim, M.C.: PS-MoM4, 1
Kim, S.I.: PS2-WeM5, 17
Kim, Y.T.: PS2-WeM5, 17
Kimura, Y.: PS1-WeA10, **22**
Kinsel, G.R.: BI+PS-FrM4, **31**
Kirmse, K.H.R.: PS1-WeA7, 22; PS2-ThM11, 28
Kita, M.: PS+TF-TuM7, 7; PS-TuP12, 14
Klick, M.: PS-ThA3, **29**
Ko, E.: PS-ThA7, 30; PS-ThA8, **30**
Koga, K.: PS+TF-TuM7, 7; PS1-WeM6, **15**; PS-TuP12, 14
Koga, T.S.: PS2-WeM8, 17
Kogelschatz, M.: PS-TuM5, **8**
Kohlstedt, H.: PS-MoA3, 5
Kojima, A.: PS-TuA5, 10
Kokkoris, G.: PS+MM-MoA8, **4**
Koo, B.-W.: PS-ThA5, 29
Koo, S.M.: PS-TuP5, **12**
Kothnur, P.S.: PS2-WeA10, **24**
Koyanagi, M.: PS+MM-MoA9, 4
Kraft, R.: PS2-ThM10, 28
Kudrja, V.: PS-TuA7, 10
Kull, K.R.: PS-ThA6, **29**
Kumar, S.: BI+PS-FrM9, **32**
Kurihara, K.: PS1-WeA4, **21**
Kushner, M.J.: PS-FrM9, 34; PS-MoM11, 2; PS-TuA8, 11
Kwon, O: PS-FrM8, **34**
Kwon, Y.S.: PS2-WeM5, 17
— L —
Lauer, J.L.: PS2-WeA7, **23**
Lazzeri, P.: PS1-WeM7, 16
Lee, D.H.: PS1-WeM8, **16**; PS-TuP2, 12; PS-WeP8, 18
Lee, G.-R.: PS+MM-MoA2, 3; PS-TuA4, **10**
Lee, J.K.: PS-WeP4, 18
Lee, J.-K.: PS+MM-MoA2, 3; PS-TuA4, 10
Lee, W.J.: PS-TuP3, 12
Lee, Y.J.: PS-WeP4, 18
Lefaucheux, P.: PS+MM-MoA7, 4; PS-WeP3, 18
Lenoble, D.: PS-ThA5, 29
Leonhardt, D.: PS1-WeA3, 21; PS-MoA9, **6**; PS-WeP10, 19
Leou, K.C.: PS1-WeM5, 15; PS-WeP1, **18**; PS-WeP11, 19
Li, M.: BI+PS-FrM4, 31
Li, N.: PS+TF-TuM5, **7**
Li, X.: PS1-ThM9, 26; PS2-ThM11, 28
Lieberman, M.A.: PS-WeP4, 18
Lin, C.: PS1-WeM5, 15; PS-WeP1, 18
Lin, T.L.: PS-WeP11, 19
Ling, L.: PS1-ThM9, 26; PS2-ThM11, **28**
Losey, L.: PS1-WeA7, 22
— M —
Madoudas, D.: PS-ThA10, 30
Mahorowala, A.P.: PS-TuA3, 10; PS-TuA6, 10
Makabe, T.: PS-TuM10, 9
Malkov, G.Sh.: BI+PS-FrM3, **31**
Malter, J.S.: PS2-WeA7, 23
Manso, M.: BI+PS-FrM6, 31; BI+PS-FrM8, 32
Mantei, T.D.: PS+TF-TuM3, **7**; PS+TF-TuM9, 8
Marletta, G.: BI+PS-FrM8, 32
Maroudas, D.: PS1-WeA8, 22
Martin, I.T.: PS1-WeA6, **21**
Mathieu, H.J.: BI+PS-FrM5, 31
Matsumura, S.: PS-ThA2, 29
McMurry, P.H.: PS1-WeM2, 15
Meger, R.A.: PS1-WeA3, 21; PS-MoA9, 6; PS-WeP10, 19
Melechko, A.V.: PS1-WeM4, 15
Mellhaoui, X.: PS+MM-MoA7, 4; PS-WeP3, **18**
Mercado, A.L.: BI+PS-FrM7, 32
Merkulov, V.I.: PS1-WeM4, 15
Meyyappan, M.: PS-MoA8, 6
Miclaus, C.: PS2-WeM8, 17
Min, J.-H.: PS+MM-MoA2, **3**; PS-TuA4, 10
Misiakos, K.: PS1-ThM2, 25
Misina, M.: PS-WeP9, 19
Mitchell, C.C.: PS-TuP7, 13
Momonoi, Y.: PS-MoA10, **6**
Mook, W.M.: PS1-WeM2, 15
Moon, J.T.: PS-MoM4, 1
Moon, S.H.: PS+MM-MoA2, 3; PS-TuA4, 10
Moravej, M.: PS2-WeA2, 22; PS-MoA7, **5**
Mori, Y.: PS2-WeA4, 23
Morioka, H.: PS-MoM6, **1**
Morita, Y.: PS2-ThM5, 27
Moshkalyov, S.A.: PS-TuA10, 11
Motika, S.A.: PS-TuM8, 9
Mukherjee, R.: PS1-WeM2, 15
Muratore, C.: PS1-WeA3, **21**; PS-MoA9, 6; PS-WeP10, 19
Muta, H.: PS-TuP10, 13
— N —
Nagahata, K.: PS2-ThM5, 27
Nagao, A.: PS2-WeA4, 23
Nakaishi, M.: PS-MoM6, 1
Nakamura, K.: PS2-WeM6, **17**; PS-ThA9, 30
Nakamura, M.: PS1-WeA4, 21; PS1-WeA9, 22; PS-ThA1, 29
Nam, B.Y.: PS-MoM4, 1
Nam, S.K.: PS-WeP12, **19**
Narendra, J.: PS-WeP16, **20**
Nestler, M.: PS-WeP15, **20**
Neumann, H.: PS-WeP15, 20
Neumann, M.: PS+TF-TuM11, 8
Nishimori, H.: PS-MoM9, 2
Nishiwaki, J.: PS-TuA5, 10
Noda, S.: PS-MoM9, **2**
Novoselov, K.: PS-TuA7, 10
Nowling, G.R.: PS2-WeA2, 22; PS-MoA7, 5
Nunes, R.W.: PS+MM-MoA1, 3
— O —
Oehrlein, G.S.: PS1-ThM9, 26; PS1-WeM7, 16; PS2-ThM11, 28; PS-FrM7, 33
Ohiwa, T.: PS-TuA5, 10
Ohmori, T.: PS-TuM10, **9**
Ohtake, H.: PS2-ThM4, **27**
Okamura, Y.: PS-TuP1, 12
Okigawa, M.: PS1-WeA5, 21
Ono, K.: PS2-WeM2, 16; PS-WeP13, 19
Orland, A.S.: PS2-WeM7, **17**
Osano, Y.: PS-WeP13, **19**
Oshikane, Y.: PS2-WeA4, **23**
Overzet, L.J.: PS-FrM2, 33; PS-FrM6, 33; PS-TuM11, 9
Ozaki, T.: PS2-ThM4, 27
— P —
Panda, S.: PS-TuA6, **10**
Pargon, E.: PS-MoM3, **1**
Park, J.H.: PS2-WeM5, 17
Park, S.D.: PS-WeP8, **18**
Peignon-Fernandez, M.C.: PS2-ThM3, 26
Perrey, C.R.: PS1-WeM2, **15**
Pokorny, P.: PS-WeP9, **19**
Posseme, N.: PS2-ThM7, **27**
Pradhan, A.: PS-MoA4, **5**
Pratoomtong, C.: PS2-WeA7, 23
Prengler, A.J.: PS-TuM11, 9
Pulpytel, J.: PS1-ThM3, 25
Pusquellic, D.: PS-TuP13, 14
— Q —
Qi, Y.: PS+TF-TuM9, **8**
Quax, G.W.W.: PS-ThA10, 30
— R —
Raballand, V.: PS2-ThM3, 26
Raja, L.L.: PS2-WeA1, 22; PS2-WeA10, 24; PS2-WeA5, 23
Ramirez, D.L.: PS2-WeM3, 16
Ramos, A.C.S.: PS-TuA10, 11
Ranson, P.: PS+MM-MoA7, 4; PS-WeP3, 18
Rasgon, S.A.: PS-TuA3, **10**
Ratner, B.D.: BI+PS-FrM1, **31**
Rauf, S.: PS-TuA7, **10**
Renault, T.: PS1-WeM2, 15
Reniers, F.: PS-WeP14, 19
Reyes-Betanzo, C.: PS-TuA10, 11
Rhiger, D.R.: PS2-WeM8, 17
Riley, M.E.: PS-TuM1, 8
Rossi, F.: BI+PS-FrM6, 31; BI+PS-FrM8, 32
Roth, D.: PS-WeP15, 20
Ruzic, D.N.: PS+TF-TuM11, 8; PS+TF-TuM5, 7
— S —
Sadeghi, N.: PS-TuM5, 8
Saitoh, T.: PS2-ThM5, 27
Sakai, I.: PS-TuA5, 10
Samukawa, S.: PS+MM-MoA9, 4; PS1-WeA5, 21; PS2-ThM4, 27; PS-MoM9, 2
Sankaran, A.: PS-FrM9, **34**
Sano, A.: PS-WeP13, 19
Sant, S.P.: PS-FrM2, 33; PS-FrM6, 33
Sasaki, T.: PS-ThA2, 29
Sato, S.: PS2-WeA4, 23
Satriano, C.: BI+PS-FrM8, **32**
Sawin, H.H.: PS-FrM3, **33**; PS-FrM8, 34; PS-MoM5, 1; PS-TuA3, 10
Schmitt, J.P.M.: PS+TF-TuM1, **7**
Schneider, St.: PS-MoA3, **5**
Scholze, F: PS-WeP15, 20
Schrauwen, C.P.G.: PS2-WeA3, 23
Setsuhara, Y.: PS2-WeM2, 16; PS-WeP13, 19
Sha, L.: PS2-WeM3, **16**
Shah, S.I.: PS1-WeM3, 15; PS-MoA4, 5
Shamamian, V.A.: BI+PS-FrM11, 32
Shen, K.J.: PS1-WeM5, 15
Shiina, T.: PS-TuP1, 12
Shiji, K.: PS-TuP11, **13**
Shim, S.I.: PS2-WeM5, **17**
Shimmura, T.: PS+MM-MoA9, **4**
Shimogaki, Y.: PS-TuA9, 11
Shin, J.: PS2-WeA1, **22**
Shin, Y.H.: PS-TuP14, 14
Shingen, T.: PS-TuP12, 14
Shinomiya, E.: PS-TuA5, 10
Shintani, K.: PS2-WeM6, 17
Shiobara, E.: PS-TuA5, 10
Shiokawa, Y.: PS-ThA1, **29**

Author Index

Shiratani, M.: PS+TF-TuM7, **7**; PS1-WeM6, 15; PS-TuP12, 14
Sho, K.: PS-TuA5, 10
Shohet, J.L.: PS2-WeA7, 23
Shohet, S.B.: PS2-WeA7, 23
Siegrist, K.: PS-TuP13, 14
Silapunt, R.: PS1-WeA7, 22
Simpson, D.J.: BI+PS-FrM9, 32
Smart, R.St.C.: BI+PS-FrM9, 32
Snyders, R.: PS1-ThM1, **25**
Soda, S.: PS+MM-MoA9, 4
Sriraman, S.: PS1-WeA8, **22**
Steen, M.L.: PS+MM-MoA1, **3**
Stets, J.R.: PS-TuM8, 9
Stevens, A.A.E.: PS-MoM7, **1**
Stout, P.J.: PS-TuA7, 10
Subramonium, P.: PS-MoM11, **2**
Sugai, H.: PS-ThA9, **30**
Sullivan, E.A.: PS+MM-MoA1, 3
Sumitani, H.: PS2-WeM6, 17
Suri, S.: PS2-ThM9, 28
Swart, J.W.: PS-TuA10, **11**
— T —
Taj, S.: PS+TF-TuM11, 8
Tajima, M.: PS-MoM6, 1
Takahashi, K.: PS2-WeM2, **16**; PS-WeP13, 19
Takase, A.: PS-TuA5, 10
Takeda, K.: PS-TuP1, 12
Takenaka, K.: PS+TF-TuM7, 7; PS-TuP12, **14**
Takeshita, K.: PS-TuM7, 9
Takeshita, M.: PS+TF-TuM7, 7; PS-TuP12, 14
Taki, M.: PS2-WeM6, 17
Talton, J.D.: BI+PS-FrM7, 32
Tan, K.M.: PS-MoM8, **2**
Taneda, Y.: PS-ThA1, 29
Tartz, M.: PS-WeP15, 20
Tatsumi, T.: PS2-ThM5, **27**
Tepavcevic, S.: BI+PS-FrM10, 32
Terahara, M.: PS-MoM6, 1
Terashima, K.: PS2-WeA8, **24**
Thomas-Boutherin, I.: PS2-ThM7, 27
Tillocher, T.: PS+MM-MoA7, **4**; PS-WeP3, 18
Timmons, C.: PS-TuM8, 9
Timmons, R.B.: BI+PS-FrM4, 31
To, B.N.: PS+MM-MoA1, 3
Tokimitsu, T.: PS-TuA9, **11**
Tomekawa, Y.: PS-TuP1, 12
Toriumi, A.: PS2-WeM1, 16
Triandafillu, K.: BI+PS-FrM5, 31
Tsai, C.H.: PS1-WeM5, 15
Tsang, C.K.: PS+MM-MoA1, 3
Tserepi, A.: PS+MM-MoA8, 4; PS1-ThM2, **25**
Tuda, M.: PS2-WeM6, 17
— V —
Vahedi, V.: PS-MoM10, 2
Vallier, L.: PS2-ThM7, 27; PS-MoM3, 1; PS-TuM5, 8
Valsesia, A.: BI+PS-FrM6, **31**
Van Assche, F.J.H.: PS1-ThM10, **26**
van de Sanden, M.C.M.: PS+TF-TuM4, 7; PS1-ThM10, 26; PS1-ThM7, 25; PS1-WeA1, **21**; PS2-WeA3, 23; PS-ThA10, 30
van Delden, C.: BI+PS-FrM5, 31
Vandencasteele, N.: PS-WeP14, **19**
Vargas-Lopez, E.: PS+TF-TuM11, 8
Varghese, P.L.: PS2-WeA1, 22
Vasenkov, A.V.: PS-TuA8, **11**
Ventzek, P.: PS-TuA7, 10
Vichiconti, J.: PS+MM-MoA1, 3
von Andrian, U.: PS2-WeA7, 23
— W —
Walton, S.G.: PS1-WeA3, 21; PS-MoA9, 6; PS-WeP10, **19**
Wang, X: PS-ThA7, **30**; PS-ThA8, 30
Wang, X.: PS1-WeM2, 15
Waser, R.: PS-MoA3, 5
Watanabe, Y.: PS+TF-TuM7, 7; PS1-WeM6, 15; PS-TuP12, 14
Wavhal, D.S.: PS-ThA6, 29
Wei, H.W.: PS1-WeM5, **15**
Wei, M.T.: PS1-WeM5, 15
Wendt, A.E.: PS1-WeA7, **22**
Williams, K.: PS-MoA2, 5
Williams, M.: PS+TF-TuM11, 8
Williams, S.: PS1-WeA7, 22
Winters, H.: PS1-WeA10, 22
Wise, R.: PS-TuA6, 10
Woen, R.V.: PS+TF-TuM4, 7
Wood, P.: BI+PS-FrM5, 31
Wu, S.J.: PS-WeP11, 19
Wu, X.: PS-TuM9, **9**
— X —
Xiao, Z.G.: PS+TF-TuM3, 7
Xu, S.: PS-MoM3, 1
— Y —
Yamada, H.: PS1-ThM11, **26**
Yamagishi, N.: PS2-WeM1, 16
Yamamura, K.: PS2-WeA4, 23
Yamasaki, S.: PS1-WeA5, 21
Yanai, K.: PS1-WeA9, **22**
Yang, X.: PS2-WeA2, **22**; PS-MoA7, 5
Ye, Y.: PS-TuM8, 9
Yeo, J.W.: PS-TuP6, **13**
Yeom, G.Y.: PS1-WeM8, 16; PS-TuP2, 12; PS-TuP3, 12; PS-WeP4, 18; PS-WeP8, 18
Yevtukhov, R.: PS-MoA2, 5
Yokogawa, K.: PS-MoA10, 6
Yoo, W.J.: PS2-WeM4, 17; PS-MoM8, 2
Yuan, X.: PS2-WeA5, **23**
— Z —
Zeuner, M.: PS-WeP15, 20
Zhang, J.: PS1-ThM8, **26**
Zhang, L.: PS1-WeM4, 15
Zhang, Y.: PS1-WeM1, **15**
Zheng, L.: PS1-ThM9, **26**
Zhigilei, L.: BI+PS-FrM7, 32
Zhou, B.: PS-FrM2, **33**; PS-FrM6, 33
Zuo, S.: PS2-WeA6, 23