Plasma Science and Technology
Room: 304 - Session PS-MoM

Plasma Etching for Advanced Interconnects
Moderator: K. Bera, Applied Materials, Inc.

8:20am **PS-MoM1 Comparison Between Hybrid and Porous Dielectric Material (SiOCH) Integration Strategies for Interconnect Technologies**, ***J. Ducote***, STMicroelectronics, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *T. Chevolleau,* CNRS-LTM, France, *S. Gall, A. Zenasni, V. Jousseaume,* CEA-LETI-MINATEC, France, *R.-L. Inglebert,* UJF-LTM, France, *C. Verove,* STMicroelectronics, France, *O. Joubert*, CNRS-LTM, France

To reduce interconnect RC delays in the future, porous SiOCH materials (p-SiOCH) are introduced as low dielectric constant materials. However, the porosity brings serious issues such as an increased sensitivity to etch and ash plasma exposures generating significant changes in the film structural properties. These issues can be aggravated by the integration strategy. One interesting emerging solutions is the late porogen removal process in which the porosity is generated by a sacrificial carbon based porogen desorbed after patterning or chemical-mechanical polishing (CMP) steps. Such hybrid materials (SiOCH matrix and porogen) are expected to be less sensitive to plasma induced damages similarly than dense low k materials. Starting from a standard damascene integration scheme, we investigate the advantages and drawbacks of hybrid materials (h-SiOCH) compared to porous materials. Etch mechanisms in fluorocarbon (FC) plasmas, material modifications induced by etching, post etch wet cleans and CMP processes are studied. Experimental results show that etching must proceed in low polymerizing chemistries since both ellipsometry and X-ray photoelectron spectroscopy (XPS) indicate an increased fluorine and carbon concentrations on the surface and lower etch rates than with porous materials. These results are well correlated with the dense nature and the high carbon content of the hybrid material both attributed to the presence of porogens. After conventional post etch wet cleans (fluorhydric acid based), no modification of the hybrid material has been evidenced thanks to infrared analyses. The impact of CMP using Hg probe measurement and IR spectroscopy has also been studied. While porous materials are modified during CMP processes due to surfactant diffusion of the slurry trough the pores, no modification is observed with hybrid materials. We have finally performed a full metal integration process and investigated the impact of the porogen removal process on the copper lines integrity. Preliminary experiment shows that copper lines are impacted by the thermally UV-assisted treatment that generates copper line corrosion issues. A promising solution, that will be presented in this paper, consist in protecting the Cu lines by a CoWP self-aligned barrier deposition and a siliciuration-nitridation process.

8:40am **PS-MoM2 Etching Characteristics of Low-k SiOCH Films by Fluorocarbon Beams: Molecular Dynamics Study**, ***A. Suzuki***, *M. Isobe,* Osaka University, Japan, *S. Kobayashi, M. Fukasawa, T. Tatsumi,* Sony Corp., Japan, *S. Hamaguchi*, Osaka University, Japan

Highly accurate control of plasma etching processes of low-dielectric-constant (i.e., low-k) insulating materials for interconnects of semiconductor chips has become increasingly important as the dimensions of transistors and interconnect wires in planer technologies diminish. In this work, in an attempt to clarify etching characteristics of SiOCH films, which are widely used as low-k materials for interconnect insulator, we have studied interaction of SiOCH films with impinging fluorocarbon beams, using molecular dynamics (MD) simulations. The simulation code and interatomic potential functions for Si, O, C, F, and H atoms are the same as those used in Ref. 1. In the simulation study presented here, we have first created model SiOCH films by depositing various monomers consisting of Si, O, C, and H atoms with low incident energies. In the numerical process of film deposition, film properties such as density, atomic composition, and porosity vary greatly, depending on the conditions used in the process. The numerical deposition processes used here were not intended to simulate actual SiOCH film formation processes but simply used to prepare model substrates that are similar to porous SiOCH films used in actual semiconductor chip manufacturing. In etching simulations, the injection energies examined in this work have been 100, 200, and 300eV. Unlike SiO2, which has the sputtering yield threshold energy at around 250eV for CF3 ion injections, numerically obtained sputtering yields for SiOCH films are significantly higher. For example, the numerically obtained Si sputtering yield (defined here as the number of Si atoms removed from the substrate surface per injection) by CF3 injections at 100eV is about 0.48. The sputtering yields for SiOCH films have been also confirmed to be an increasing function of the incident energy. We have also examined the sputtering yield dependence on (1) the film density and also (2) incident beam species varying from F to CFx with x = 1~4. For the latter, at 100eV, the dependence on the value x is found to be rather weak.

[1]T. Takizawa, et al., AVS 54th International Symposium & Exhibition, October 14-19, 2007, PS1-MoM2.

9:00am **PS-MoM3 Plasma Challenges of Porous SiOCH Patterning for Advanced Interconnect Levels**, ***T. Chevolleau***, CNRS/LTM France, *T. David, N. Posseme,* CEA/LETI/D2NT France, *M. Darnon,* CNRS/LTM France, *F. Bailly,* CEA/LETI/D2NT France, *R. Bouyssou,* CNRS/LTM France, *J. Ducote,* CEA/LETI/D2NT France, *L. Vallier, O. Joubert*, CNRS/LTM France **INVITED**

In CMOS technology, one of the dominant strategies to achieve future generation of ultra low-k interlayer dielectric (ILD) materials with a dielectric constant close to 2.2 is to introduce porosity into a SiOCH matrix. For the integration of porous SiOCH in damascene structures, the most important challenges are: 1) to manage profile control of narrow features (sub-75 nm trenches and vias), 2) to minimize the plasma-induced damages (modification and surface roughness) and 3) to prevent barrier diffusion into the porous SiOCH. In this work, we will address the damages (modification and surface roughness) induced by the etching and ashing plasmas on both blanket and patterned wafers. The film modification and surface roughness induced by fluorocarbon, reducing, and oxidizing plasmas have been characterized by using infrared spectroscopy, ellipsometry, atomic force microscopy techniques. The results will be presented and discussed in terms of mechanisms of film modification and formation of surface roughness. Experiments will also focus on the profile control of narrow p-SiOCH trenches using different masking strategies (metal hard mask versus organic mask). Plasma etching conditions have been optimized for both type of mask approaches to achieve sub-75 nm patterns using scanning electron microscopy and chemical topography analyses by X-ray photoelectron spectroscopy. We have shown that the organic hard mask exhibits better patterning capability in terms of trench profile control. The use of metallic hard mask can lead to profile distortion and process drift induced by metal contamination on the patterned structures and on the reactor walls of the etcher, respectively. Post etching treatments like reducing (NH_3, H_2/He, CH_4…) and oxidizing (O_2) plasmas have also been investigated on both blanket and patterned wafer to limit the barrier diffusion. We have shown that the barrier diffusion can be strongly limited if the ashing plasma generates a modification and densification of the p-SiOCH material surface. In conclusion, a delicate trade-off has to be found between the modification of the porous SiOCH film and the limitation of the barrier diffusion in order to minimize the increase in k value.

9:40am **PS-MoM5 Plasma Damages on Organic Low-k Film due to VUV Radiation, UV Radiation, Radicals, Radicals with Radiation, and Ions in H_2/N_2 Plasma Etching Processes**, ***K. Takeda***, *S. Takashima, R. Saito, S. Uchida,* Nagoya University, Japan, *M. Fukasawa, K. Oshima, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan, *M. Hori*, Nagoya University and JST-CREST, Japan

The low dielectric constant (low-k) films are widely introduced as interlayer dielectrics for ULSIs. An organic low-k film, polyallylene (PAr), is one of prospective candidates for interlayer films with low-k. PAr receives the damages from the plasmas. The plasma damages induce the increase of the dielectric constant of the films. In our previous studies, we have developed the novel technique for evaluating the damages due to radiation, radicals and ions in plasmas separately (Pallet for plasma evaluation : PAPE) and clarified the generation mechanism of porous SiOCH films using the PAPE in plasma etching using H_2 and N_2 gases.[1] In this technique, a vacuum ultraviolet (VUV) window, an ultraviolet (UV) window, a Si plate, or nothing were placed on low-k films and were irradiated by plasmas. Therefore, we can evaluate the influence of individual VUV radiation, UV radiation, radicals, radicals with radiations, and ions on the damage of films. In this study, the damage induced by H_2/N_2 plasma was investigated to clarify the generation mechanism of surface changes due to VUV radiation, UV radiation, radicals, radicals with radiation, and ions on the organic low-k films. The dual frequency capacitively coupled plasma apparatus for 8 inch wafer processing was used in this study. VHF (60MHz) and bias (2MHz) powers of 500 W were applied to the upper and the bottom electrodes, respectively. The pressure of H_2 and N_2 mixture gas was 5.3 Pa. The etching time was 20 s. At a gas flow rate ratio of 50 %, the etching depth of the sample irradiated by radiation, radicals, and ions was approximately 80 nm. The other samples on the conditions without ion bombardment were not etched and the refractive index of the sample irradiated by radiation, radicals, and ions increased significantly compared to the other samples, which indicated that the damages caused by ions were greater than those due to VUV, UV radiation, and radicals. On the other

hand, in the pure N_2 plasma, the thicknesses and refractive indexes of all samples were not changed. From these results, the damage caused by the ion bombardment was suppressed by surface nitriding of organic low-k film due to N_2 plasma exposure. On the basis of results, the generation mechanism of damage is presented.

[1] S. Uchida, S. Takashima, M. Fukasawa, K. Ohshima, K. Nagahata, T. Tatsumi , and M. Hori, J. Appl. Phys., 103 (2008) 073303.

10:20am **PS-MoM7 Impact of Reducing and Oxidizing Post Etching Plasma Treatments on Porous SiOCH Integration**, ***R. Bouyssou***, *T. Chevolleau,* CNRS-LTM, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *J. Ducote,* STMicroelectronics, France, *L. Vallier, J. Joubert*, CNRS-LTM, France

For 45 nm interconnect technology node and beyond, porous SiOCH (p-SiOCH) materials with porosity higher than 25% and a dielectric constant lower than to 2.5 are being introduced. However the porosity brings serious integration issues such as a high sensitivity of porous materials to etching and ashing plasma exposures and the risk of metallic precursor diffusion into the dielectric during conformal barrier deposition. This work focuses on the development of post etching plasma treatments using reducing and oxidizing chemistries. Such plasma treatments can be used as i) ashing processes and/or ii) post cleaning processes (wafer and/or reactor walls) and/or iii) "pore sealing-like" processes to prevent metal barrier diffusion. p-SiOCH wafers (porosity of 26% and k=2.35) prepared by plasma enhanced chemical vapour deposition have been etched and post etched in a dual frequency capacitive reactor. Plasma induced modifications of p-SiOCH have been investigated both on blanket and patterned wafers using volume and surface analyses techniques such as infrared spectroscopy (in transmission and in multiple internal reflexion), ellipsometry (spectroscopic and porosimetric), x-ray photoelectron spectroscopy and water contact angle. For each chemistry (NH_3, H_2, CH_4 and O_2), we have optimized the plasma conditions minimizing the p-SiOCH modifications such as carbon depletion, new bonds formation (Si-H, Si-OH,..) and moisture uptake. After methane based plasma treatments (CH_4/N_2) a carbon rich layer (a few nanometers thick) presenting hydrophobic properties is deposited on the p-SiOCH surfaces. After NH_3 and O_2 based plasmas, the surface becomes hydrophilic and carbon free. Infrared analyses show no moisture uptake after CH_4 based plasmas while a significant amount of water uptake is detected after NH_3 and O_2 plasmas. Furthermore, dielectric constant (k) measurements after the different plasma treatments demonstrate that the k increase is strongly related to the formation of silanol groups and moisture uptake. The capabilities of the plasma treatments presented in this study to remove post etch-residues from the p-SiOCH surface and to prevent the barrier diffusion into p-SiOCH will be also addressed.

10:40am **PS-MoM8 Effects of Plasma Etch and Ash Processes on Porous Low-k Film Surfaces in a Dual-Damascene Flow**, ***C.B. Labelle***, Advanced Micro Devices, Inc., *D. Horak,* IBM Research, *Y. Zhou, A. Li, K. Zhou, C. Zhang, R. Patz, A. Darlak, J. Pender*, Applied Materials, Inc.

Porous ultra low k dielectrics ($k < 2.4$) are being integrated into current and future technology nodes. As film dielectric values are driven lower, new interactions are observed between the films and the plasma etch environments to which they are exposed. Some of these interactions are extensions of the chemical sensitivities previously observed for k=2.4 materials (i.e., plasma ash damage), while others are a result of the change in the microstructure of the films as additional porosity is incorporated to decrease dielectric constant (i.e., pore size, pore connectivity, etc.). Post-etch and ash film surface roughness has often been observed with porous dielectrics and the etching and ashing process window to achieve a smooth dielectric surface decreases as the porosity increases. In this work, post-etch and/or ash film surface roughness effects will be examined for several different structures. The focus of the work is on a k=2.2 porous carbon doped oxide film utilizing a via first trench last integration scheme. Surface roughness phenomena are observed both on planar and vertical surfaces. In some cases, plasma modification to the film from one step is only observed several steps beyond the damage point. The sensitivity of the film requires careful control of every step of every plasma exposure to minimize cumulative and/or combinatory effects. Results will be presented highlighting some of the process spaces explored. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:00am **PS-MoM9 Mechanisms of Residue Formation on TiN Hard Mask after Patterning of Porous SiOCH Films in Fluorocarbon-Based Plasma**, ***N. Posseme***, CEA-LETI, France, *T. Chevolleau, R. Bouyssou,* LTM-CNRS, France, *T. David,* CEA-LETI, France, *V. Arnal, N. Jourdan, S. Doloy, C. Verove,* ST Microelectronics, France, *O. Joubert*, LTM-CNRS, France

For the 45 nm interconnect technology node, the introduction of porous SiOCH materials (p-SiOCH) brings major concerns such as the sidewall modifications induced by ashing plasmas used to strip the photoresist. Metallic hard mask (MHM) integration avoids exposure of the porous SiOCH films to resist stripping plasmas but generates its own set of issues such as metal contamination of the patterned structures. In particular, the growth of metallic residues on the MHM is often observed after p-SiOCH etching in fluorocarbon (FC) plasmas. Since, these defects are not removed after wet cleans, they directly impact the electrical performance measured on via chains. This work focuses on the mechanisms of residue formation on metallic hard mask (titanium nitride, TiN deposited by Physical Vapor Deposition) when exposed to FC based plasma etching. In situ post-etch plasma treatments have also been investigated as potential solution to remove these defects. The mechanisms of residue formation have been investigated using different analyses techniques such as ex-situ x-ray photoelectron spectroscopy (XPS), scanning electron microscopy cross section and energy dispersive x-ray (EDX). These experiments have been performed on TiN blanket wafers deposited on 200 nm thick SiO_2 layers and on patterned wafers etched in a dual frequency capacitive etcher. The growth of residues on metallic hard mask is observed when the wafer is etched in FC plasmas and exposed to air. EDX and XPS analyses both show that these residues are TiF_x like residues. We have also observed that the kinetic of residue formation after air exposure on metal hard mask is correlated with the etching chemistry (SF_6, C_xF_y, ...), the plasma operating conditions (w or w/o ion bombardment), the chemical composition of the etched materials (SiO_2, p-SiOCH, SiCN) and moisture content. Based on these results, the mechanisms of the residues formation will be presented and discussed.

11:20am **PS-MoM10 BEOL Pattern Flop Over as a Challenge to Shrink Feature Critical Dimension Continuously**, ***Y. Yin***, *J.C. Arnold,* IBM Corporation, *T. Sparks,* Freescale Corporation, *P. Basler, S. Schmitz*, IBM Corporation

As feature critical dimension (CD) shrinks toward the limit of Moore's law, many problems, including pattern flop over, become serious challenges in the Back-End-Of-Line (BEOL) plasma etch development. A clear understanding of the origin and control of pattern flop over is extremely desirable since it will cause failure in product development. BEOL pattern flop over is due to several different reasons. One of the root causes is the high Aspect Ratio (AR) of mask/dielectric lines. As the technology node moves from one generation to the next, the feature pitch size shrinks faster than the feature vertical dimension (trench/via depth) to allow the integration density to increase. Consequently, mask/dielectric lines with higher AR in BEOL are required. When the AR exceeds the critical value (approximately 3) flop over can happen very easily. The mask/dielectrics lines bend over and sometimes touch each other. Different flop over phenomena have already been observed at 22 nm node look-ahead research. Photoresist feature delamination has been noted post resist development because of the smaller pitch size. Two of the most significant mechanisms, mask flop over and dielectrics flop over, occur during the plasma etching process. The soft organic materials in the litho stacks can bend over and lead to mask flop over when the AR is high. This flop over partially shadows the trench and forms distorted dielectric lines. The dielectrics line itself can also flop over at high aspect ratios, which is most likely due to a combination of high AR and low material strength. In addition, wet treatment post plasma patterning can cause significant flop over due to capillary forces. One of the possible ways to avoid pattern flop over, is to improve the mechanical properties of the mask and dielectric materials. With our research efforts, we hope we can understand and solve this challenge in time to move closer toward the limit of Moore's law.

Plasma Science and Technology
Room: 304 - Session PS-MoA

Invited Highlights on Plasma-Surface Interactions - Honoring the Distinguished Career of Herbert H. Sawin
Moderator: J.P. Chang, University of California, Los Angeles

2:00pm **PS-MoA1 Plasma Etching - The Early Days**, ***J.W. Coburn***, University of California at Berkeley

Remarkable progress has been made in the implementation and understanding of the pattern transfer capabilities of plasma etching in the 30 or so years this technique has been used in microelectronics manufacturing. Where did it all begin? One perspective of some of the early highlights introduced in the mid-1970s will be presented. The importance of studies supporting physical sputtering (both sputter-etching and sputter-deposition) using Ar glow discharges will be emphasized. A select few pioneering advances in processing chemistries will also be described.

2:20pm **PS-MoA2 Following Moore's Law – How Many Knobs are Enough?**, ***R.A. Gottscho***, *K. Smekalin*, Lam Research **INVITED**

With the introduction of 3x technology, more new materials are introduced into semiconductor devices and their manufacture. Yet, the basic etch challenges do not change qualitatively: selectivity, profile, uniformity, damage, line edge roughness and more. Quantitatively, of course, virtually everything changes: with each shrink, the difficulty in meeting the tolerances increases along with cost. The tightening of tolerances on the die, the wafer, and the system places un-precedented demands on system and sub-system variability reduction – active and passive. For repeatable, high yield, high output manufacturing, minimizing variability is essential. Yet the requirements to shrink stimulate increased demands for more control "knobs." Some knobs are provided to compensate for asymmetric limitations in design or inherent non-uniformities. Other knobs are provided to expand process flexibility in the hope of facilitating recipe optimization. The irony is that more control knobs means increased variance in the control parameter vector leading directly to more difficulty in matching chambers and narrower process windows, leading to more manufacturing excursions and downtime. More control knobs also means more recipe complexity. Despite impressive advances in simulation capability, plasma process development remains an empirical endeavor. With the most recent advances in etch production equipment, the number of recipes that have a measurable impact on the wafer are already more than 1 trillion. Can any production recipe be said to be truly optimal? Do more control variables help or hinder our ability to meet next-generation technology challenges? And do they save cost or add cost?

3:00pm **PS-MoA4 Real Time and 3D Characterization Techniques to Control Plasma Etch Processeses at the Nanometer Scale**, ***O. Joubert***, CEA/LETI-Minatec, France

As the industry approaches the ability to create microcircuit structures on the order of 20 nm, this technology faces fresh challenges. To make progress, we need to go back to the basic science of how plasmas interact with surfaces. Several trends are at work: First, circuit patterns need to be accurate to within 1 nm and below, within a single wafer and across several wafers. Second, plasma etching is becoming an integral part of pattern generation (using lateral erosion of the lithographic photoresist to improve resolution, for example). Third, aspect ratios of the final structures (that is, the ratio of length to width) are increasing dramatically. Finally, the number of potential new material candidates and their possible combinations in future structures is exploding. In this context, understanding the fundamentals of the etch mechanisms and their correlations to key process parameters is crucial. Each etch step must be characterized not only by etch rate and uniformity, but also by more fundamental properties such as the composition, thickness, and line-edge roughness of the sidewall layers of the structure, the chemical nature of etch by-products deposited on the chamber walls (which affects process stability and reproducibility), the thickness of the etch-front mixing layer (correlated to etch rate and selectivities between layers), and the impact of aspect ratio–dependent etching phenomena. In this talk, we will describe in details the latest development in scatterometry that can be used to monitor in real time resist trimming processes or more complex processes. We will also discuss the latest results obtained using the 3D AFM technique to characterize the transfer of photoresist line edge roughness in complex stacks. Finally we will also discus the importance of monitoring passivation layers formed on the feature sidewalls as well as the coatings formed on chamber walls during plasma processes since both impact directly the critical dimension of patterned structures.

3:20pm **PS-MoA5 Investigations of Plasma-Polymer Interactions For Nanoscale Patterning of Materials[1,2]**, ***G.S. Oehrlein***, University of Maryland

The combination of photolithographic patterning of organic materials followed by plasma-based transfer of photoresist patterns into electronic materials enables the production of nanometer scale devices required in information technology products. Despite the success of these thin film and substrate patterning approaches in what is possibly the most important example of nanoscale manufacturing, important gaps in our scientific understanding of relevant plasma-polymer interactions remain. In this talk we will review chemical and morphological changes induced in selected model polymers and advanced photoresist materials as a result of interaction with fluorocarbon/Ar plasmas. Of special interest are the changes of the materials that take place at the beginning of the plasma-polymer interaction period. We will evaluate the respective roles of a) polymer structure/chemistry and b) plasma process parameters on the consequences of the plasma-polymer interactions. The impact of plasma-induced polymer alterations on changes of polymer-defined nanoscale features will also be discussed.

[1] Based on collaborations with S. Engelmann, R. L. Bruce, F. Weilnboeck, T. Kwon, T.C. Lin, R. Phaneuf, Y. C. Bae, C. Andes, D. Wang, D. Graves, D. Nest, J. Vegh, E. A. Hudson, B. Long, G. Willson, P. Lazzeri, E. Iacob and M. Anderle

[2] We gratefully acknowledge financial support of this work by the National Science Foundation under awards Nos. DMR-0406120, DMR-0705953 and NIRT CTS-0506988.

4:00pm **PS-MoA7 Will Recombination Reaction Probabilities at Plasma Chamber Walls Ever Be Non-Adjustable Parameters?**, ***V.M. Donnelly***, University of Houston

Reactions of neutral species on surfaces immersed in plasmas have been recognized for many years to be an important class of processes that plays a major role in determining the make-up of species in the plasma. The association of radicals on the surfaces of chamber walls and substrates represents a sink for radicals and a source of larger product species. Chemistry-rich models have been developed in recent years for plasmas such as those used to etch silicon and dielectric materials. Heterogeneous reactions are an essential part of these models. With the exception of a few atom recombination reactions, the reaction probabilities for these processes are completely unknown; hence they are usually treated as adjustable parameters, or are guessed at and left constant. Experimental measurements of these reactions are usually carried out in one of two ways, neither is ideal. First, in-situ measurements can made in the plasma. This approach has the advantage of studying the surface that exists during plasma operation - one that is often coated with amorphous deposits of sputtered or etched substrate and reactor materials, and receives high fluxes of neutrals, ions, electrons and photons. This complexity makes it difficult to isolate individual reactions. Consequently, a second approach has been practiced in which the complex plasma environment can be avoided by studying reactions in high vacuum with selected molecular beam impingement. While this approach can provide accurate measurements of reaction probabilities, product identification and surface characterization, it can also lead to misleading predictions when extended to real plasma conditions. This talk will briefly review a few selected studies that highlight the complexity and lack of consensus in this field, and offer prospects for system-non-specific rate parameters for this class of heterogeneous reactions.

4:20pm **PS-MoA8 Ion-Surface Interactions Beyond Etching**, ***K.P. Giapis***, California Institute of Technology

Plasma etching has been conceptually distinguished into physical and chemical etching, in reference to the way material is removed from the surface under ion bombardment. There are other ion-surface interactions at play, which have received little attention although they may substantially alter the outcome of the etching process—especially when patterning wafers. We will present evidence from ion beam experiments for the following mechanisms: 1) Eley-Rideal (abstraction) reactions, 2) Electronic excitation as a result of inelastic collisions, 3) Pre-dissociation of molecular ions before collision with the surface, and 4) Coulomb explosion of adsorbed electronegative atoms. The importance of these processes in plasma etching will be discussed.

4:40pm **PS-MoA9 Can Plasma Modeling Be a Predictive Tool in Process Development?: Etching of Very High Aspect Ratio Features and Gate Stacks***, *M. Wang, Y. Yang, J. Shoeb,* ***M.J. Kushner***, Iowa State University

The use of modeling in the development of plasma tools has achieved a significant degree of success. Optimizing the uniformity and energies of reactant fluxes with results of modeling prior to prototyping by varying, for example, the aspect ratio of the reactor or frequency of excitation is now accepted practice. The assist of modeling to develop plasma processes has provided a less clear return on investment. This is due, in part, to the complexity of the reaction mechanism and the lack of fundamental data. The rate of technology development will likely outstrip our ability to generate the required fundamental data, at least in the near term. As such, what are the realistic expectations for modeling to provide high value to the development of plasma processes? In this talk, the general status and the potential success of plasma modeling in the development of processes will be discussed with results from two case studies using reactor and feature scale modeling platforms. In the first, sporadically occurring twisting of via-like features in extremely high aspect ratio etching has been attributed to the stochastic nature of fluxes entering the feature as the size of the opening shrinks. This is an effect exacerbated by charging. Here the reaction mechanism, fluorocarbon plasma etching of Si and SiO_2, is relatively well known. So modeling has assisted in developing a dc-augmented strategy for the capacitively coupled tools that addresses the contribution of charging to twisting. In the second, high-k dielectric HfO_2 gate stack etching, the reaction mechanism is at best poorly known. Here, the contribution of modeling has been to refine that reaction mechanism based on the existing but fragmentary database and so narrow the now broad range of operating conditions that might be considered in process development.

*Work supported by the Semiconductor Research Corp., Micron Inc., Applied Materials Inc. and Tokyo Electron Ltd.

5:00pm **PS-MoA10 Predictive Etch Profile under Competition Among Deposition, Etching, and Charging on Dielectrics in a Low Temperature Plasma**, ***T. Makabe***, Keio University, Japan

A dielectric surface exposed to plasma irradiation keeps competitive, physical and chemical processes among etching, deposition, and charging on the local pattern.[1] Top down plasma nano-etching is a technology assisted by a directional and energetic positive ion onto a surface saturated by adsorbed chemical molecules. The ion flux to the wafer has a magnitude of $10^{15}cm^{-2}s^{-1}$. It means that the ion incident on the surface transfers the kinetic energy to the lattice with a relaxation time shorter than the surface collision interval. We have no way to protect the surface from the charging damage, particularly on the dielectric, in a periodically steady state radio frequency (rf) plasma, which always forms the positive ion sheath in front of the biased wafer to be etched. We have demonstrated a technique to inject negative charges having a relatively high energy in a synchronized mode between an rf plasma source with on/off period and a LF bias pulse in order to develop a charging free plasma etching. It is realized by an artificial formation of a double layer close to the wafer.[2,3] The synchronized pulsed operation will enable us to develop a charging free plasma etching. The time constant of local charging, caused by the great difference in the velocity distribution between ions and electrons incident on a topographical surface, is approximately two orders of magnitude shorter than the time for the effective monolayer etching in SiO_2. This difference enables us to estimate the etching profile by the two-step evaluation, i.e., surface charging followed by etching. Even in a controlled wafer exposed to a plasma etching, the surface is the competitive processes between etching and deposition, where two-layer model will be efficient in order to predict the feature profile evolution by using Level set method[3]. Predictive images are shown and discussed for the feature profile evolution of dielectric.

[1] T. Makabe and Z. Petrovic, “Plasma Electronics: Applications in Microelectronic Device Fabrication”, Taylor & Francis (2006).

[2] T. Ohmori, T. Goto, T. Kitajima, and T. Makabe, Appl. Phys. Lett. 83, 4637-9 (2003); T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696-3709 (2008).

[3] T. Shimada, T. Yagisawa, and T. Makabe, Japan J. Appl. Phys. 45, L132-4 (2006); Ibid. 45, 8876-82 (2006); T. Makabe, T. Shimada, and T. Yagisawa, Comp. Phys. Commun. 177, 64-7 (2007).

5:20pm **PS-MoA11 Silicon Processing Technologies in Adjacent Spaces: Applications Beyond Information Technology**, ***T. Dalton***, IBM

Over the course of the last fifty years, the microelectronics industry has made tremendous strides in the development and manufacturing of ever more complex integrated circuits (IC). These circuits have typically been applied to the information technology (IT) industry and have driven improvements in the computational power per dollar of many orders of magnitude. Part of the “toolbox” of skills acquired to produce integrated circuits is the ability to form desired patterns at ever decreasing sizes. The minimum controllable feature size has been reduced by six orders of magnitude (from millimeters to nanometers) during the last fifty years. With feature sizes rapidly approaching 10nm, the conventional silicon IC industry is nearing a threshold with the end of conventional silicon scaling approaching. Research today focuses on new device structure to replace the CMOSFET as the engine of the IT industry. Another very active research area is the concept of taking the skill-set acquired from IC research, development, and manufacturing, and to apply those skills into new area – “adjacent spaces” where the ability to machine patterns at very small sizes may open up new areas of research and development, and to form the basis for future industries.

Plasma Science and Technology
Room: 304 - Session PS-TuM

Advanced Gate Etching
Moderator: Y. Zhang, IBM

8:00am **PS-TuM1 High Density Plasma Etching of Titanium Nitride Metal Gate Electrodes for FDSOI Sub-Threshold Transistor Integration**, ***S.A. Vitale***, *J. Kedzierski, N. Checka, C.L. Keast*, MIT Lincoln Laboratory

Dual work function band-edge metal gate electrode materials are replacing polysilicon gates at the 45nm technology node for high performance CMOS logic production. At the same time, mid-gap metal gate electrodes are being considered to replace polysilicon gates in novel fully depleted silicon-on-insulator (FDSOI) ultra-low power CMOS devices. A discussion of the physical and electrical requirements of the gate materials for these two technologies will be presented, along with an introduction to the "gate first" vs. "gate last" integration approaches. Titanium nitride metal-gated capacitors and transistors have been successfully fabricated, on a conventional SiO2 gate dielectric. C-V curves have been measured and fit to a quantum-corrected model, with a measured workfunction of 4.55eV. Gate oxide breakdown data reveals a charge-to-breakdown approximately 10x lower than that of conventional polysilicon/SiO2 gates, and a discussion of how this may be improved using a HfO2 high-k gate dielectric will be presented. A key challenge of integrating metal gates is the plasma etching of the gate stack. Conventional etching of a polysilicon layer above the TiN results in a large foot at the base of the polysilicon, due to the presence of the conducting TiN film. TiN etch selectivity over SiO2 in excess of 40:1 is achieved by measuring and exploiting the difference in ion enhanced etching threshold energy between these films. TiN is shown to etch spontaneously in HBr plasmas due to the thermodynamically favorable Ti + Br reaction, but is strongly inhibited in the presence of oxygen. TiN etching in high density plasmas exhibits a strong aspect ratio dependent etching (ARDE) effect, which can be minimized by using a two-step etch process, with different neutral-to-ion flux ratios. *This work was sponsored by the Air Force under contract #FA8721-05-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the author and are not necessarily endorsed by the United States Government.

8:20am **PS-TuM2 TaN Etch Mechanisms in BCl_3-based Plasmas**, ***D. Shamiryan***, IMEC, Belgium, *A. Danila,* Moscow Institute of Electronic Technology, Russia, *V. Paraschiv, M.R. Baklanov, W. Boullart*, IMEC, Belgium

TaN is a potential candidate for metal gates. BCl_3 plasma is used to pattern metal gates as it has high selectivity over Si substrate and etches metal oxides (native oxides on metal gates and high-k dielectrics). During metal gate etch in inductively coupled plasma reactor, we found that TaN gate profile depends on the composition of BCl_3-based plasma. Pure BCl_3 results in an undercut of TaN. The undercut can be avoided by addition of 5% O_2, further increase of O_2 concentration (till 10%) does not change the TaN profile. When N_2 is added to BCl_3 plasma, first the undercut disappears (at about 6% of N_2) and then a slope appears as N_2 concentration increases further (toward 10%). To clarify the etch mechanisms, we studied etching of blanket TaN wafers (30 nm film deposited by PVD). To avoid ion bombardment and simulate conditions on the sidewalls of a gate, the substrate bias was set to zero. Etch rate of TaN was measured by spectroscopic ellipsometry; surface composition was examined by XPS. In the case of pure BCl_3 plasma a thick film (deposition rate of 20 nm/min) is formed. The film consists of B (50%), Cl (30%) and O (20%). The oxygen probably comes from the oxidation on air between the etching and the XPS measurements. When 5% of O_2 is added, no film is observed, the surface composition is close to as-deposited TaN (with some B added). We observed strong peaks in emission spectra of BCl_3/O_2 plasma, attributed to BO_x. When 5% N_2 is added to the BCl_3 plasma, a film of the same thickness as for pure BCl_3 is observed, but it contains less Cl (15%). We propose the following etch mechanism. In pure BCl_3 plasma a Cl-containing film is deposited on the sidewalls of the gate. Cl from the film reacts with TaN producing an undercut. When O_2 is added, no film is formed and the TaN profile is straight as B apparently reacts with O in the gas phase, forming volatile BO_x radicals. Further increase of O_2 content does not change the profile as no film is formed (until O_2 concentration reaches 50% when B_2O_3 film is deposited). When N_2 is added to BCl_3, a film is formed but in this case N_2 replaces Cl and the film becomes passivating leading to a straight TaN profile. As more N_2 added, the film passivates TaN more efficiently leading to a sloped profile.

8:40am **PS-TuM3 Etching Profile Simulation of Metal/High-k Dielectric HfO_2 in Chlorine Based Chemistry**, ***T. Yagisawa***, *T. Makabe*, Keio University, Japan

With continuous downscaling of complementary CMOS devices, the physical thickness of SiO_2 gate dielectric is requested to be reduced to sub-micrometer regime. When the thickness is less than 1 nm, gate dielectric cannot satisfy the requirement of the low standby power CMOS devices beyond 32 nm technology node in 2013, due to the increase of gate leakage current, poly-Si gate depletion, and dopant penetration into the channel region. In order to overcome these issues, extensive studies to replace conventional poly-Si/SiO_2 with metal/high-k gate stack have been carried out. Among several candidates, HfO_2 attracts considerable attention because of its thermal stability at the interface with Si. It is well known, chlorine based chemistry is more suitable for the plasma etching of high-k dielectric HfO_2 than fluorine chemistry due to the high volatility of the etched by-products. One of the most promising procedures to etch metal/HfO_2 gate stack is Cl_2/O_2 plasma where high selectivity can be obtained over underlying Si and SiO_2. In addition, the etching residues made of Hf chloride may not be volatile in a low temperature condition. This leads to a significant adsorption at the sidewall, resulting in a variation of surface roughness (LWR: line width roughness). Thus, the etching profile of high-k material has strong dependence on substrate temperature. In this paper, the etching profile of high-k HfO_2 film is numerically predicted in the chlorine based chemistry in a two-frequency capacitively coupled plasma. Dependence of LWR on the substrate temperature will be mainly discussed by considering the redeposition of etched by-products ($HfCl_xO_y$) inside the pattern. Emphasis will also be given on the selectivity of HfO_2 etching over Si and SiO_2.

9:00am **PS-TuM4 Reaction Mechanisms in Patterning Hafnium-Based High-k Thin Films**, ***R.M. Martin***, *J.P. Chang*, University of California, Los Angeles

As hafnium-based oxides are being implemented into sub-45nm CMOS devices, the corresponding development of an enabling plasma etching chemistry is necessary for patterning these new gate dielectric materials. In this work, an electron cyclotron resonance high density plasma reactor was used to study the etching of hafnium aluminates and nitrided hafnium silicates with varying compositions in chlorine-based chemistries. In general, the measured etch rate for these materials scaled with the square root of ion energy at high ion energies (> 50 eV), however the etch rates in BCl_3 was 4 to 7 times that in Cl_2, due to the change in the dominant ion from Cl_2^+ to BCl_2^+. The composite oxides were found to etch faster than the simple oxides, and had roughly 2 eV lower etching threshold energies. The etching threshold energy can be tuned by the film composition, making it possible to maximize the etching selectivity with respect to the gate and substrate materials. A generalized etch rate model was formulated based on the competing etching and depositing mechanisms involved in complex plasma chemistries, as determined from analysis of the experimental data , while the etch rate dependencies on neutral-to-ion flux ratio and ion energy were correctly represented. This surface site balance based approach accounts for competition between depositing and etching species with a steady-state overlayer, and employs proper assumptions for different chemistries at various energy regimes. The model fitted well to the experimental data under various ion energy and chemistry conditions, specifically, it was able to account for the transition between physical- and ion-enhanced etching in Cl_2 plasmas and the transition between deposition and etching in BCl_3 plasmas, as the ion energy increased. As quantitative information pertaining to high-k etching behavior can be extracted from this model, it is possible to extend its applicability to predict the etching characteristics of new materials in related plasma chemistries.

9:20am **PS-TuM5 Etch Challenges at the 22nm Node and Beyond**, ***R. Turkot***, Intel Corporation **INVITED**

As semiconductor manufacturing marches along according to its roadmap, the challenges of plasma etch at and around the transistor continue to increase. The last few generations have shown continued success to scale transistor gate lengths and simultaneously introduce novel transistor architectures with existing plasma etch technologies. Increasing numbers of new materials and continued scaling of material thicknesses and CDs promise to keep the pressure on plasma etch to deliver innovative solutions. Selectivities to multiple novel, thinner materials will be required. Etch tool environments may experience dramatic changes from traditional silicon or oxide etches and require "re-learning" of proper cleaning and conditioning. Even analysis of the structures being created becomes increasingly difficult as we march forward. Continued vigilance to the understanding of plasma etch and early identification of novel innovations to pattern, analyze and

sustain integrated solutions across research, development and manufacturing is paramount to the success of plasma etch at the 22nm node and beyond.

10:40am **PS-TuM9 Etch Mechanisms of Silicon Gate Structures Patterned in SF_6/CH_2F_2 Inductively Coupled Plasmas**, ***O. Luere***, Freescale Semiconductors, France, *L. Vallier, E. Pargon, O. Joubert*, LTM-CNRS, France

Patterning sub-40 nm gates presents several challenges among which maintaining a tight CD control is one of the most challenging. To succeed, understanding the etching mechanisms in gate patterning processes is one of the challenge. In this work we have investigated the different physical phenomena involved during the patterning of silicon structures in SF_6/CH_2F_2 based plasmas. The experimental work has been carried using a 200 mm etch platform connected, under vacuum, to an x-ray photoelectron spectroscopy surface analysis system. We have studied the impact of the SF_6/CH_2F_2 ratio on the silicon etch rate, thickness and composition of the reactive layer formed on the bottom silicon surfaces of the etched structures, thickness and composition of the sidewall passivation layer formed on the silicon sidewalls and silicon profiles. Our results demonstrate that there are very good correlations between the silicon etch rates and reactive layers formed on the bottom silicon surfaces. Contrary to previous studies performed using $HBr/Cl_2/O_2$ chemistries our results indicate that there is no simple correlation between the thickness of the CF_x passivation layer formed on the sidewalls and the final slope obtained in silicon. Our results demonstrate on the contrary, that even if very thin CF_x based passivation layers are formed on the silicon sidewalls, significant slopes can be generated in silicon. Other experimental results will be shown to elucidate the etch mechanism driving the silicon gate etch profiles during SF_6/CH_2F_2 plasma etching.

11:00am **PS-TuM10 Reduction of Si Recess during Gate Etching with RLSA Microwave Plasma Source**, ***T. Mori***, *M. Sasaki, T. Nishizuka, T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

As the design rule of ULSI devices continue to be scaled down, the critical dimension (CD) and reduction of silicon recess will need to be precisely controlled.[1] In this study, poly gate etching was evaluated to reduce silicon recess with RLSA (Radial Line Slot Antenna) microwave plasma source. RLSA generates plasma just below top dielectric plate, and as the plasma diffuses forward the wafer, its density and electron temperature become low immediately. The gate stack which was used for experiments consisted of SiN/Poly/Gate-Ox (2nm)/Si. First, it was etched with Vdc=-150V and Si recess was observed with TEM by changing over etching percent 50%, 100%, and 150%. The profile of gate stack was getting straight as increasing over etching percent and Si recess was less than 1.1nm. Second, by optimizing etching condition with lower Vdc=-135V, Si recess was 0.8nm and the profile kept straight. We suppose not only Vdc but also plasma potential Vp are effective factor to reduce silicon recess since the maximum ion energy can be estimated by adding plasma potential and Vdc. Comparing Vp under the same bias power between RLSA and RF plasma by ion energy analyzer on the chamber wall, it was found that RLSA plasma had lower Vp than RF one. RLSA can provide low Vdc and Vp condition keeping gate stack straight. This unique plasma characteristics will be able to use post 22 nm node Si etch like 3D gate that needs less etching damage on Si surface.

[1] S. A. Vitale and B. A. Smith, J. Vac. Sci. Technol. B 21, 2205 (2003).

11:20am **PS-TuM11 Effect of Inductively and Capacitively Coupled Plasma Pulsing on Charging of Features in Plasma Etching**, ***A. Agarwal***, *P.J. Stout, S. Banna, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma charging damage presents challenges to maintaining critical dimensions during plasma etching of high aspect ratio (HAR) features (aspect ratio > 50). In one form of process induced charging damage, charge retention at the bottom of trenches can lead to breakdown as the accumulated charge stresses the material and creates a weak path for the injected current.[1] Charging damage occasionally manifests itself as tapering and twisting of HAR features, where the via or trench turns from the vertical to oblique direction.[2] This behavior is erratic in nature due to the randomness of the ion and radical flux composition as the feature dimensions approach only a few tens of nm. Polymer deposition on the sidewalls during dielectric etching can trap charge, which leads to less than ideal profiles. Neutral beam etching[3] (decreased interaction of charged particles with feature) and UV photon bombardment[4] (which increases surface current and conductivity allowing charge to drain through) have been suggested as useful techniques to mitigate charging damage. Pulsed plasma operation of an inductively or capacitively coupled plasma reactor may also allow for control of charging damage if negatively charged species can be extracted from the plasma. In this paper, pulsed and continuous plasma operations will be compared for etching in electronegative plasmas using results from a computational investigation. A 2-dimensional plasma equipment model (HPEM)[2,4] has been linked to a Monte Carlo feature profile model[5] to assess the consequences of pulsed plasma operation on charging of features. Results will be discussed for source and bias pulsing in an ICP reactor for poly-silicon etching and for pulsing of dual frequency CCP reactor for dielectric etching. Pulsed plasma operation allows for reduced interaction of charged species and depending on the mode of operation may allow for electrons to overcome the sheath potential thus neutralizing the accumulated charge. Sustaining a steady pulsed plasma can however be complicated in strongly electronegative gas mixtures as the plasma may not reignite after power is turned off.

[1] T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696 (2008).
[2] A. Agarwal, M.M. Wang, and M.J. Kushner, 54th AVS Symposium 2007.
[3] D.J. Economou, J. Phys. D 41, 024001 (2008).
[4] K. Rajaraman, Ph.D. Thesis, Univ. of Illinois (2005).
[5] P. Stout, 60th Gaseous Electronics Conference 2007.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+PS+AS+BI+SS-TuA

Plasma-deposited Polymer and Organic Surfaces in Biological Applications
Moderator: E.R. Fisher, Colorado State University

1:40pm **BO+PS+AS+BI+SS-TuA1 High Throughput Surface Chemical Analysis of Polymer Microarrays: Wettability, Protein Adsorption and Cell Response Correlations***, M. Taylor, A.J. Urquhart,* The University of Nottingham, UK*, Y. Mei, D.G. Anderson, R. Langer,* MIT*, M.C. Davies,* ***M.R. Alexander***, The University of Nottingham, UK **INVITED**

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,[1] to on-slide polymerisation as microarrays in nano-litre volumes.[2] Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.[3] The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.[4] Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.[5] The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

[1] Brocchini S et al. Structure-property correlations in a combinatorial library of degradable biomaterials. Journal of Biomedical Materials Research 1998 42 66.

[2] Anderson DG, et al. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. Nature Biotechnology 2004 22 863.

[3] Urquhart AJ, et al. High throughput surface characterisation of a combinatorial material library. Adv Mats 2007 19 2486.

[4] Urquhart AJ et al. TOF-SIMS analysis of a 576 micropatterned copolymer array to reveal surface moieties that control wettability. Anal Chem 2008 80 135.

[5] Taylor M et al. A Methodology for Investigating Protein Adhesion and Adsorption to Microarrayed Combinatorial Polymers. Rapid Macromol Comm 2008 (in press).

2:20pm **BO+PS+AS+BI+SS-TuA3 Plasma Medicine***,* ***A. Fridman***, Drexel University **INVITED**

Novel engineering and science approaches sustaining human health, such as for example radiation biology and laser medicine, represent a significant segment of technological developments around the world. Recent breakthrough discoveries of the highly energetic but non-damaging direct treatment of living tissues with non-thermal plasma enable to create new branch of the engineering medicine, PLASMA MEDICINE, which creates qualitatively new possibilities of healing, treating of previously untreated diseases, deactivation of dangerous pathogenic organisms, development of new direct methods of medical diagnostics. New types of non-thermal atmospheric plasma discharges are able to operate directly contacting human body and other living tissues, which significantly increase effectiveness of the tissue sterilization, treatment of wounds, skin and other diseases, as well as direct medical diagnostics. Obviously success of the plasma medicine depends on deep fundamental understanding of physics, chemistry and biology of the non-thermal plasma interaction with living tissues, and engineering of the relevant non-thermal plasma discharges, which is to be discussed in the presentation. Recent achievements in plasma biotechnology also address many aspects of the challenging problem of deactivation of viruses and bacteria that cannot be disinfected by traditional methods. Disinfecting large volumes of air in buildings and hospitals economically is now possible with room-temperature atmospheric pressure plasma. Similarly, atmospheric plasma technology can be employed to sterilize medical equipment, clothing, and building walls; to disinfect living tissue without side effects, and to disinfect and preserve food and water without damage. In addition, plasma technology can also be used to create innovative tools for sensing, detection and identification of dangerous pathogenic organisms as well as to characterize success of the cleansing processes. Essential advantage of the plasma biotechnology is its potential for universal availability, due to the technology's exclusive reliance on electrical power. It avoids many logistical difficulties associated with delivery, storage and disposal that typically hinder chemical and pharmaceutical approaches to sustainable health. Plasma technology can also be easily scaled from point-of-use devices to centrally operated plants capable of cleaning massive quantities of material. The key element of recent plasma technology developments is its use as a catalyst of many natural biological processes. As such, plasma can provide highly energy efficient treatment of biological materials, which is also to be discussed in the presentation.

3:00pm **BO+PS+AS+BI+SS-TuA5 Plasma Polymer Patterning of PDMS for Microfluidic Application***,* ***S. Forster****, A.G. Pereira-Medrano, M. Salim, P.C. Wright, S.L. McArthur*, University of Sheffield, UK

Microfluidic systems are becoming increasingly important for a wide range of bioengineering applications including proteomics and protein separations. Polydimethylsiloxane (PDMS) has proved to be the most popular material for microfluidic device production in the laboratory due to its many advantages over traditional materials. However, PDMS has some fundamental problems, namely a lack of functionality present at the surface, high protein fouling and inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of specificity and sensitivity in many bioassays. Plasma polymerisation is a method of depositing a uniform polymeric coating onto a surface, while retaining the desired functionality of the monomer. Hence, plasma polymerisation presents a versatile approach for surface modification and patterning of device channels. The wide range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple surface properties within a single device are required. The aim of this work was firstly to investigate methods to produce stable plasma polymer patterns on PDMS. The coatings chosen include acrylic acid and maleic anhydride for their functional groups and tetraglyme to reduce non-specific protein adsorption. Patterning using photolithographic techniques and subsequent specific biomolecule immobilisation was achieved. Surface characterization using XPS and ToF-SIMS was used to ensure the spatial, chemical and biomolecule resolution of the device surfaces produced. This ability to combine microfluidics with spatially defined reactive regions on a 'non-fouling' background was then used in a number of applications to show the diversity and efficiency of the devices. Protein digestion by immobilized trypsin using single flow-through experiments in PDMS devices was improved using plasma polymer functionalized channels. The results achieved using mass spectrometry showed an increase in speed and sensitivity of the digestion as well as superior device reliability. Finally, plasma functionalized channels were used to investigate the effect of ampholyte adsorption onto device walls in isoelectric focusing (IEF). By coating channels with a tetraglyme plasma polymer an increase in sensitivity and reproducibility of IEF measurement was achieved. This technique can also increase the 'lifetime' of the device by ensuring channel properties were unchanged.

4:00pm **BO+PS+AS+BI+SS-TuA8 Plasma Etching for Selective Removal of PMMA from nm-scale PS/PMMA Block Copolymers for Lithographic Applications***,* ***A.E. Wendt****, Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpsel,* University of Wisconsin-Madison*, P.F. Nealey*, University of Wisconsin, Madison **INVITED**

Diblock copolymers films, in which polymer components segregate into nano-scale domains, have been shown to have tremendous potential in fabrication of nm-scale surface topographies. Applications range from microelectronics fabrication to the study of how topography affects the growth and behavior of living cells or microorganisms. Use of block copolymers as a template for pattern transfer requires selective removal of one polymer component, and has motivated our study of plasma etching of polystyrene (PS) and polymethyl-methacrylate (PMMA), the two components of the PS-PMMA diblock copolymer. To better understand the mechanisms of the etch process for these materials, we have surveyed the effects of etch gas mixture and ion bombardment energy (taking advantage of our capability to produce a narrow ion energy distribution at the substrate), in combination with chemical analysis of the resulting etched surfaces. Of particular interest are the mechanisms of surface roughening, which shows a complex dependence on plasma process conditions that is not easily explained. A review of the literature on factors contributing to surface roughness, such as intrinsic inhomogeneity in the film, local deposition/micro-masking, shadowing effects and redeposition will be presented. We ultimately propose a mechanism for roughening of PS that involves micro-masking by inhomogeneous modification of surface chemical composition (rather than deposition) in oxygen-containing plasmas. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

4:40pm **BO+PS+AS+BI+SS-TuA10 Correlation of Macroscopic Surface Qualities of Poly-Parylene with Plasma-Specific Parameters**, ***G. Franz***, *F. Rauter, M. Häge*, University of Applied Sciences, Germany

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivates of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.[1,2] Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF_4 (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.[3] The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O_2 generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

[1] H.K. Yasuda, and Q.S. Yu; J. Vac. Sci. Technol. A 19, 773 (2001)

[2] Q. Yu, C.E. Moffitt, D.M. Wieliczka, and H. Yasuda; J. Vac. Sci. Technol. A 19, 2163 (2001)

[3] A.D. Tserepi, M.-E. Vlachopoulou, and E. Gogolides; Nanotechnology 17, 3977 (2006).

5:00pm **BO+PS+AS+BI+SS-TuA11 Plasma Processing of Nanostructured Polymeric Surfaces for the Development of Immunosensors**, *A. Valsesia,* ***P. Colpo****, I. Mannelli, G. Ceccone, F. Rossi*, European Commission Joint Research Centre, Italy

Immunosensors play a very important role for the development of Point-of-Care analysis thanks to their rapid and sensitive detection capabilities.[1] Among others, the control of the interface between the transducer and the biological probes is a crucial issue since the bio-interface is the essential element that guaranty the bioactivity of the immobilized biological probes.[2] The control of the bio-interface is typically addressed by functionalizing the surface with special chemical groups. Besides, new nanobiotechnology-based tools have led to more sophisticated approaches that use for instance nanostructured surfaces. Benefits have been already shown in terms of the improvement of immunoreaction efficiency.[3] In this work we propose a new method for fabricating nanostrucured surfaces combining the use of colloidal masks with different plasma processes. In this method, Plasma Polymerization Processes are able to produce pinhole-free functional layers with different properties. The choice of the precursor together with the appropriate plasma processing parameter ensures the production of stable functional layers which can be used for the production of the chemically contrasted nanopatterns. Also the deposition of the colloidal mask in a controlled way is essential: for example, mass sensitive detectors (like Quartz Crystal Microbalance, QCM) require the use of very large areas in order to obtain measurable signals. Also plasma etching plays a very important role: it is important to choose the suitable processing parameters enabling the fabrication of nanostructured surface which are not limited in the patterning geometry and resolution. After the optimization of the nanofabrication process, the surfaces of immunosensors have been nanostructured. In particular we transferred the nanostructures on the crystals of QCM for on-line monitoring of the protein adhesion. The nanostructures accelerate the kinetics of absorption and increase the density of absorbed molecules, resulting in higher bioactivity of the immobilized proteins and consequently in an improvement of the immunosensing performances.

[1] K. R. Rogers, Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology 2000, 14, 109-129.

[2] B. Kasemo, Current Opinion in Solid State and Materials Science 1998, 3, 451-459.

[3] A. Valsesia, P. Colpo, T. Meziani, P. Lisboa, M. Lejeune, and F. Rossi, Langmuir 2006, 22, 1763-1767.

5:20pm **BO+PS+AS+BI+SS-TuA12 Use of Multivariate Analysis Techniques to Predict Cellular Response to Plasma Polymerized pNIPAM**, ***J.E. Fulghum****, K. Artyushkova, A. Lucero, H.E. Canavan*, University of New Mexico

The primary objective of this work is to investigate the correlate structural properties of a thermoresponsive polymer, poly(N-isopropyl acrylamide) (pNIPAM), with its ability to reversibly adhere cells. PNIPAM undergoes a sharp property change in response to a moderate thermal stimulus at physiological temperatures (~32 °C). This behavior has generated great interest in the biomaterials community, and pNIPAM is being investigated as a "smart" release coating to harvest intact cell monolayers. Many techniques are used to deposit pNIPAM, including electron beam irradiation and solution deposition (e.g., silanes and self-assembled monomers). Recently, we constructed a radio frequence (rf) plasma reactor for plasma polymerization of NIPAM (ppNIPAM) from the vapor phase based on a previous design. Plasma polymerization is a sterile, solvent-free, and compatible with surfaces of any geometry or chemistry. These factors make plasma polymerization extremely useful for cell and tissue culture, which often rely on plastic tissue culture plates. Due to the inherently energetic conditions of the plasma, parameters such as maximum rf wattage, location/position of the samples in the chamber, and monomer flow have on the resulting films. In this work, pNIPAM films resulting from those varying conditions are characterized using X-ray photoelectron spectroscopy (XPS) for film composition, interferometry for film thickness, contact angles for thermoresponse, and cell detachment for cell releasing properties. Using multivariate analysis, the structural information of the films obtained at various polymerization conditions will be correlated with their thermoresponsive and cell-releasing behavior. In this way, we will predict the conditions that will optimize film composition for bioengineering applications.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+PS-TuA

Photovoltaics
Moderator: B.J. Stanbery, Helio Volt Corporation, J. Xue, University of Florida

1:40pm **EN+EM+NS+PS-TuA1 Thin films, Plasmas and Solar Cells**, ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands **INVITED**

Solar cells, devices which can convert sunlight directly into electricity by the photovoltaic (PV) effect, is now recognized as one of the options to provide a significant fraction of the energy mix in 2050 to power the world. Presently the PV industry is booming and two important challenges lie ahead: increasing the efficiency of conversion of sunlight into electricity and obtaining the required scale in terms of the surface area produced. The latter requires high throughput processing of solar cells in all its aspects. Increasing the efficiency is scientifically attaining the most attention, but history has shown that more cost reduction can be obtained by improving processes and increasing the scale of the industry. This talk will address both challenges by discussing the role of thin film and plasma technology. Presently the solar cell market is dominated by solar cells based on crystalline silicon. In this solar cell technology, where the photo-active material is wafer based silicon, thin films still play an important role to increase efficiency by effectively passivating bulk and surface defects and enhancing light trapping in the solar cell. The high rate deposition of a-SiNx:H as passivation and anti-reflection coating, by means of the expanding thermal plasma technique, will be shortly reviewed. Possible combinations with novel concepts to convert the solar spectrum will be addressed. Recently, we also introduced plasma assisted atomic layer deposition of Al_2O_3, a high k dielectric containing a large amount of negative charge, to passivate future p-type emitters on n-type silicon based solar cells. Demonstration of improved performance of n-type solar cells using this type of passivation layer with an efficiency as high 23.2 % will be discussed. To obtain the required large scale by 2050 further improvement of thin film solar cell technology will be essential, both in terms of materials as well as in terms of processes. Apart from the need for high throughput deposition of the photo-active materials, additional thin film technologies will be needed for barrier layers on substrates to limit impurity transport, for efficient light trapping (textured surfaces and anti-reflection layers) and last but not least encapsulation layers to guarantee the lifetime of the thin film solar cell. Apart from the further development of improved materials and device concepts, process monitoring and control to improve quality and throughput becomes more and more important. I will discuss here the monitoring of high rate deposition of microcrystalline silicon by means of optical emission spectroscopy. This optical probing method also

enables the in situ detection of the crystallinity of the material deposited as well as fundamental insights in the growth mechanism.

2:20pm **EN+EM+NS+PS-TuA3 Effects of Nanostructures formed by Plasma Etching on Reflectance of Solar Cells**, ***S.H. Ryu***, *C. Yang, W.J. Yoo,* Sungkyunkwan University, Korea, *D.-H. Kim, T. Kim*, Samsung Advanced Institute of Technology, Korea

We investigated the lithography-free plasma etching methods to modify surface of single crystalline Si which was widely used for manufacturing of solar cells. Experiments were performed using SF6/O2 gases dry etching for the purpose of reducing the reflectivity at the Si surface. Upon inductively coupled plasma etching in SF6/O2 pillar-shaped nanostructures were formed on the surface which changed to black in color. The absorption factor was estimated by measuring reflection and transmission on the surface across near UV to near IR. Before etching, reflectance of Si wafer was ~ 35% in the wavelength range of 600-1000 nm and > 50% in the wavelength range of 200-400nm, whereas it decreased to < 5% after performing SF6/O2 plasma etching. The absorption factor of Si wafer after etching was increased up to ~ 90% from 65% compared to that without etching, in the wavelength range of 600-1000 nm. Furthermore, various etching methods and conditions to suppress reflectivity in a broad spectral range were investigated for optimization of the surface property of the solar cells, ie, enhancement of solar cell efficiency. We investigated the effects of various processing parameters on surface property by changing gas ratio, bias power and etching time. The current-voltage characteristics on the surface textured solar cells showed that short circuit current (Isc) and open circuit voltage (Voc) changed sensitively depending on the surface treatment. The relation between the surface morphology and the absorption factor was analyzed.

2:40pm **EN+EM+NS+PS-TuA4 Nanoscale Heterojunction Engineering to Grow High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt***, *J. Sheng, T.E. Vandervelde,* University of New Mexico, *J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories, *S.M. Han*, University of New Mexico

In an effort to reduce the manufacturing cost of multijunction solar cells, we have scaled up a process to grow low-defect-density Ge films on 2-inch-diameter Si substrates. This growth technique makes use of nanoscale heterojunction engineering to minimize the interfacial strain density. The engineered substrates may potentially replace the Ge wafers that are currently used in multijunction solar cell fabrication, if the Ge film's bulk and surface quality can match that of the epi-ready Ge wafers. We will present results for the scaled-up process of Ge film production, including key aspects of the nucleation process and film characterization, using transmission electron microscopy and etch pit counting. Next, we present our efforts to produce a high-quality surface finish, using chemical-mechanical planarization, and method for cleaning and passivating the Ge surface. Additionally, results of GaAs film growth on our engineered substrates will be presented and compared to growth on Ge and GaAs wafers, both offcut and nominal. We find that the offcut wafers effectively eliminate anti-phase domains in the GaAs. We also observe room-temperature photoluminescence from GaAs epilayers grown on our engineered Ge/Si substrates. Lastly, future work and directions will be discussed in light of our findings.

3:00pm **EN+EM+NS+PS-TuA5 On a New Concept of Tandem Photovoltaic Cells Based on III-V Semiconductor Materials**, ***M. Emziane,*** Masdar Institute of Science and Technology, UAE, *R.J. Nicholas*, University of Oxford, UK

We have investigated single-junction and double-junction photovoltaic devices using ternary and quaternary InGaAs(P) semiconductor materials. These were designed and optimized for potential applications in conventional photovoltaics, thermophotovoltaics and concentrator photovoltaics.Different bandgaps were considered for single-junctions, and various bandgap combinations were simulated for the top and bottom cells of the tandem devices where the structure comprises two single-junction cells connected back to back and separated by a middle common contact. For both single and double-junctions, the device structures were modeled and optimized as a function of the doping concentration and thickness of the active layers, and the simulations show that optimum device performance can be achieved by using relatively thin structures and low doping concentrations in the emitter and base layers. The variation of the device performance with the black-body source temperature, incident intensity and operating temperature was also simulated and discussed. Due to the split of the incident spectrum, the bottom cell response is found to be different from that expected for a single-junction cell having the same bandgap. The optimal bandgap combination that delivers the best total efficiency for the tandem device was also determined and the data discussed.

4:00pm **EN+EM+NS+PS-TuA8 Thin Film Preparation of Chalcopyrites for Solar Cells and Fundamental Material Physics**, ***S. Siebentritt***, University of Luxembourg **INVITED**

Thin film solar modules are expected to be the next generation of photovoltaics technologies. Their cost reduction potential has been estimated much higher than that of Si wafer technologies. Among the various thin film technologies solar cells based on chalcopyrite ($CuInGaSe_2$, CIGS) absorbers show the highest efficiencies, reaching 19.9% in the lab. These record solar cells are prepared by a high vacuum co-evaporation process that proceeds in three stages with different composition. A simplified two stage co-evaporation process is used in the first mass production of chalcopyrite solar modules. Further industrial processes are the sputter deposition of metallic precursors which are reacted in an annealing process to the semiconductor compound. Recently electrochemical deposition has appeared as a low cost approach to the precursor deposition. In all cases the knowledge on fundamental growth processes, nucleation behaviour and detailed reaction is limited. The details of the processes and their advantages and disadvantages for solar module production will be discussed. The afore mentioned deposition processes result in polycrystalline films with grain sizes of approximately 1 micrometer. For the investigation of the fundamental material physics it is necessary to obtain grain boundary free material. The lattice mismatch between $CuInSe_2$ and $CuGaSe_2$ on one side and GaAs on the other side is between 2.2 and -0.7% and allows epitaxy of chalcopyrite films on GaAs. Several methods for the epitaxy have been developed: metal organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and a hybrid sputter/evaporation process. The specifics of these processes will be briefly discussed and some results of epitaxial films will be presented.

4:40pm **EN+EM+NS+PS-TuA10 Influence of a Single Grain Boundary on Epitaxial $CuInSe_2$ Film Growth**, ***A.J. Hall***, *D. Hebert, A. Rockett*, University of Illinois at Urbana-Champaign

Very large multigrain copper indium diselenide (CuInSe2) films were grown on gallium arsenide (GaAs) multigrain wafers using a hybrid sputtering/effusion growth process. Scanning electrom microscopy (SEM) morphology shows excellent epitaxial grain growth on the substrate with intimate grain boundary contact. Electron backscatter diffraction analysis shows a crystal misorientation common axis and misorientation angle for a high-angle, non-twin, boundary. Atomic force microscope and transmission electron microscope images are presented which confirm the surface morphology and the atomic intimacy of the grain interface. Kelvin probe force microscopy shows that the grain-boundary has little electrical influence on the film in comparison to other features present in the crystallites. Growth of large multicrystalline or bicrystalline CuInSe2 films allows more careful study of both physical and electrical influence of grain-boundaries on film properties. Current work on the physical influence of a single boundary on film growth is discussed.

Plasma Science and Technology
Room: 304 - Session PS-TuA

Fundamentals of Plasma-Surface Interactions I
Moderator: K.P. Giapis, California Institute of Technology

1:40pm **PS-TuA1 Examining Sidewall Formation, Passivation, and Etching in Nanometer-Scale Feature Fabrication using Molecular Dynamics Simulation**, ***J.J. Végh***, *D.B. Graves*, University of California, Berkeley

A firm understanding of fundamental etch limitations is becoming increasingly important as the scale down of feature sizes continues in the manufacture of semiconductor and other thin-film devices. Molecular dynamics (MD) simulations have been conducted to model the formation of small (~2-3 nm) features in silicon, both through the use of confined beams of ions and radicals and through exposure of a substrate to ions and radicals through an explicit masking layer. We compare simulations using an amorphous carbon mask on top of the silicon substrate to other simulations assuming a perfectly confined beam of bombarding species (i.e. to mimic a mask) on the same geometry (~2 nm wide trenches). The presence of the masking layer strongly affects the overall etch process and the minimum achievable feature size. For example, material from the mask is seen to sputter into the feature, where it mixes with the substrate material, and subsequently affects the etch yield and chemistry. Likewise, material from the substrate is seen to sputter and redeposit on the sidewalls of the mask, affecting sticking and transport of subsequent incident species. Ion scattering off the walls of the mask also affects the etch process by altering the angle of incidence and energy of the ions that hit the substrate. For certain bombarding chemistries, the masking layer shows severe

degradation and loss of structural fidelity. We illustrate how this loss of fidelity in the masking layer transfers to the underlying substrate material on the small scales examined. The role of sidewall passivating radicals vs. the role of ions (i.e. CF_x at 300 K vs. 200 eV CF_X^+ ions) is also examined: data on sticking coefficients and scattering probabilities are presented and the relative contributions from ions and radicals to the final sidewall composition are elucidated. Ion bombardment alone is sufficient to form a ~1 nm thick damaged/passivation layer along the sidewall, but deposition from radicals also plays an important role in determining the ultimate sidewall structure as the features deepen. We also discuss the challenges of extending MD to include larger and more realistic systems and other important effects, including substrate charging, long-timescale diffusion, and alternative masking materials such as SiC, etc.

2:00pm **PS-TuA2 What are the Limiting Factors for Etching sub-10nm Si Holes?**, ***Y. Zhang**, E.M. Sikorski, B.N. To*, IBM Research

Patterning transferring nanometer-scale semiconductor features with precision has pushed us to think of the 'true' limits for plasma etching. One of the possible limits plasma etching facing is what the smallest holes (vertical side wall holes) plasma etching can do. In this paper, we report the recent results of studying plasma etching of nanometer-scale features with a focus on sub-10nm holes into silicon substrates as an examples to study the possible 'limits' for pattern transferring by plasma etching. Using diblock copolymer self assembled nanometer-scale patterns as starting templates, we using different methods to shrink the dimensions of the nanometer-scale holes down to sub-10nm regime. We studied plasma etching challenges for etching nanometer-scale holes into silicon with different masks in different plasma chemistries and process conditions. The results indicate that the plasma chemistry, plasma conditions and parameters, substrate temperatures, and the characteristics of aspect ratio dependence all play roles in the etching processes of forming nanometer-scale holes in silicon substrates. Among all the factors, when hole diameters shrinking down to sub-10nm regime, the sidewall passivation formed during the etching of holes with vertical sidewall becomes the determining factor for how small holes can be etched into silicon substrates. The result agrees with the previous studies.[1,2] The impacts of mask materials and selectivity to etch sub-10nm holes will be also discussed.

[1] Y. Zhang, Plasma Etching of Nanoscale Features, http://meetings.aps.org/link/BAPS.2007.DAMOP.C3.3, Calgary (2007).

[2] J. J. Végh and D. B. Graves, Investigating Fundamental Etch Limits: Molecular Dynamics Simulations of Sub-10 nm Feature Fabrication, AVS 54th International Symposium, http://www2.avs.org/symposium2007/Papers/Paper_PS2-WeM11.html.

2:20pm **PS-TuA3 Three Dimensional Modeling of Surface Profile Evolution During Plasma Etching (Plasma Prize Lecture)**, ***H.H. Sawin****, Massachusetts Institute of Technology **INVITED**

We have developed a profile simulator capable of modeling both feature scale evolution as well as roughening within the feature during plasma etching. As roughening is inherently a three dimensional phenomenon, we chose to extend our 2.5D Monte Carlo simulation with cellular surface position and composition representation to a full 3D simulation. The surface interaction is computed based on a local polynomial fitting of the surface cells and computing the surface kinetics based upon the particle interaction with this curved surface. An algorithm for addition and removal of cells was developed based upon a balance between adding cells which retain a smooth surface and the addition of cells which advance the surface in the direction of the local surface normal. The simulation was tested against a broad range of conditions and shown to satisfactorily model feature scale profile evolution. To model the surface kinetics, we used a moving mixed surface layer description in which the surface kinetics are based upon the composition in the cell(s) upon which the particle strikes as well and the incident. The kinetics included incident angle dependence with respect to the polynomial's normal, the energy dependence of ion bombardment, and the etching yield dependence on surface curvature. Ion scattering with dispersion about the specular scattering angle of ions as well as dispersion of scattered neutrals and disperse emission of reaction products. Redeposition of reaction products was included as well. With this model, we have successfully simulated the roughening of Si surfaces under Ar ion bombardment demonstrating the creation of surface striations oriented transverse to the direction of ion bombardment at low off-normal angles, smooth surfaces at intermediate off-normal angles, and striations parallel with the ion bombardment at higher incident angles. We have also simulated the transition from transverse to parallel roughening which occurs with increased etching time. We have also successfully modeled oxide and low-K dielectric etching using surface kinetics developed for oxide etching with fluorocarbon discharges.

* 2008 Plasma Prize Winner

3:00pm **PS-TuA5 3-Dimensional Monte Carlo Simulation and Experimental Measurements of Surface Roughness under Plasma Etching**, ***W. Guo**, H. Kawai, H.H. Sawin*, Massachusetts Institute of Technology

Surface roughening on poly-Si, SiO_2 and various low-k dielectrics were experimentally measured and modeled in the 3-Dimensional Monte Carlo profile simulator as a function of etching chemistry, ion incidence angle and amount of etching time. Experimental data and modeling results were in good quantitative agreement in terms of etching yield and roughness level, suggesting the incorporated mixing-layer kinetics model is able to accurately account for the chemistry taking place on various substrates and plasma chemistries. Morphologically, all films displayed transverse striation at intermediate ion angle, and parallel striation at grazing ion angle in Ar sputtering or low polymerizing C_4F_8/Ar chemistry. The transition from transverse to parallel striation at different ion angles were captured with the profile simulator by combining the curvature-dependent sputtering with surface diffusion suggested by B-H model, through which the impinging ions deliver more energy to the surface in depressions relative to elevations. It was demonstrated experimentally and in modeling that the ripple formation is sensitive to the amount of etching: transverse striation on single-crystal Si at 60˚ion angle gave way to parallel striation as etching persisted. The surface roughening mechanism at grazing angle at 75˚ ion angle was proposed as the micromasking mechanism which effectively roughens the surface with both clean net-etching region and sporadically polymer-rich net-deposition region. The modeled elemental composition was mapped on the surface and compared to the experimental data to disclose the roughening mechanism.

4:00pm **PS-TuA8 Scaling Relationships of Polymer Surface Roughening with Energy Density and Surface Composition during Plasma Processing**, ***S. Engelmann**, F. Weilnboeck, R.L. Bruce, G.S. Oehrlein,* University of Maryland, College Park, *C. Andes,* Rohm and Haas Electronic Materials, *D.B. Graves, D.G. Nest,* University of California, Berkeley, *E.A. Hudson*, Lam Research

The modifications of 193nm and 248nm PR blanket materials, patterned structures, and model polymers during and after plasma etching were studied using ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, and scanning electron microscopy. The plasma parameters examined include bias power, source power and pressure in C_4F_8/90% Ar discharges. In addition, CF_4/Ar chemistries (0-100% Ar) have been examined. We combined these widely varying plasma conditions in a model addressing the photoresist roughening behavior in oxide etch plasmas. The roughness evolution was based on a transfer mechanism by ions and a characteristic roughening behavior based on the energy density present on the PR surface during processing. We found that in our discharges this roughening behavior scales linearly with the energy density present at the surface during the discharge, suggesting an overriding importance of the molecular structure on the roughening behavior. A proportionality of this scaling based on the molecular structure of the PR material was noted. The resulting surface roughness can be predicted if the polymer structure, exposure time and the energy density during plasma processing are known. We also found that the energy density of the surface could be greatly reduced by an increase in etch yield. The etch yield could be effectively increased depending on the oxygen and fluorine surface coverage of the PR material. Our results indicate that either high removal or high roughening occurs during plasma processing, but both parameters cannot be independently optimized.

4:20pm **PS-TuA9 Plasma VUV-induced Degradation of Polymer Films: Effects of Radiation Wavelength**, ***D.G. Nest**, T.-Y. Chung, J.J. Vegh, D.B. Graves*, University of California at Berkeley, *S. Engelmann, F. Weilnboeck, R.L. Bruce, T.C. Lin, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park, *B. Long, G. Willson,* University of Texas, Austin, *E.A. Hudson,* Lam Research Corp., *C. Andes, D. Wang*, Rohm and Haas Electronic Materials

A fundamental understanding of roughening mechanisms of polymer materials used in pattern transfer during plasma processing is of increasing importance as device dimensions continue to shrink. We have shown that vacuum ultraviolet (VUV) radiation, ion bombardment, and heating all play important roles in the roughening of photoresist materials. In this study, we further investigate the role of VUV radiation in the degradation of polymer materials. Exposure to VUV radiation results primarily in the loss of carbon-oxygen bonds in the bulk of PMMA-based polymers, such as 193-nm photoresists. However, the VUV spectrum impacting the substrate depends on the processing conditions and especially on the gas composition. In a vacuum beam apparatus, we exposed PMMA-based photoresist to VUV radiation from various gases using a remote inductively coupled plasma. The radiation from the source was calibrated spectrally. The range of VUV radiation wavelengths responsible for polymer

degradation was isolated using various VUV transparent windows and implications for polymer processing are discussed.

4:40pm **PS-TuA10 Plasma Radiation Effects on Photoresist Degradation and Depth Fluorination of Photoresists in Fluorocarbon Discharges**, ***F. Weilnboeck**, S. Engelmann, R.L. Bruce, G.S. Oehrlein,* University of Maryland, *D.G. Nest, D.B. Graves,* University of California, Berkeley, *C. Andes, D. Wang,* Rohm and Haas Electronic Materials, *E.A. Hudson*, Lam Research Corp.

The influence of radiation generated by Ar and Ar/C_4F_8 plasmas on the material degradation of photoresists (PR) is studied. Blanket films of fully formulated 193nm and 248nm PR were exposed to different radiation spectra, ranging from visible to vacuum ultraviolet light. Radiation was filtered by placing the PR underneath a structure containing transparent windows with different cut-off wavelengths, i.e. borosilicate glass (310nm) or MgF_2 (120nm). Thickness changes, chemical and morphological evolution of the PR surface were characterized using Ellipsometry, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). It was found that 193nm PR is highly sensitive to radiation wavelengths between 120nm and 310nm while 248nm PR was unaffected. The evolution of surface roughness and bulk material modifications with time was also analyzed by AFM and FTIR, and will be reported. Furthermore, we investigated the effect of bulk fluorination in 193nm and 248nm PR materials. Previous observations point towards material dependent differences of fluorination depth in the bulk for materials exposed to fluorocarbon plasmas. This phenomenon is poorly understood and will be addressed by exposing the PR materials to a C_4F_8/90%Ar discharge followed by depth profiling. Results will be presented at the meeting.

5:00pm **PS-TuA11 Ar Ion Sputtering of GaAs Studied by Molecular Dynamics Simulation and Laser Spectroscopy of Ga Atoms in the Gas Phase**, ***E. Despiau-Pujo****, *P. Chabert,* LPTP, CNRS - Ecole Polytechnique, France, *R. Ramos, G. Cunge, N. Sadeghi*, LTM, CNRS - UJF - INPG, France

III-V compounds such as GaAs or GaN-based materials are increasingly important for their use in optoelectronic applications, especially in the telecommunications industry. Photonic devices including lasers, photodetectors or LEDs, require reliable dry etching processes characterized by high etch rate, profile control and low damage. Recently, inductively coupled plasma-reactive ion etching (ICP-RIE) has been used to etch GaAs and its alloys.[1] Due to its high plasma density, ICP-RIE generally results in a high ion flux with moderate ion energies. However, ion bombardment during the etching process can damage the material and lead to amorphisation at high doses. Molecular dynamics (MD) simulations of GaAs sputtering under low-energy Ar ion bombardment were recently developed by Despiau-Pujo et al.[2] This study showed that a significant fraction of Ga products leave the surface with more than 10% of the incident ion energy. The aim of the present work is to verify the simulation predictions and measure the velocity distribution function of Ga sputtered atoms. We describe the operation of a GaN laser diode at 403.3 nm for the spectroscopy of Ga atoms in an ICP argon discharge. To obtain both perpendicular and longitudinal velocity components, LIF measurements are performed in z direction and atomic absorption spectroscopy in x direction. Ga atoms are sputtered from the wafer surface by energetic ions produced in the Ar buffer gas of an industrial ICP etch reactor (LAM 9400). The external cavity diode laser is tested and tuned on resonance with Ga transition. For various pressure and ion energy conditions, we perform a systematic study of the Doppler-broadened LIF and absorption spectra to extract perpendicular and longitudinal velocity distributions of sputtered Ga atoms. At very low pressure, these distributions are compared to sputtering theory and MD results. We observe a good agreement between MD predictions and experiment, even if simulations tend to overestimate the perpendicular velocities of sputtered atoms. These results confirm the existence of products sputtered from the surface with significant energies, which constitutes a key point since these atoms could alter passivation layers on sidewalls during etching, and be responsible for defects observed in nanodevices.

[1]Y. Matsukura et al, J. Vac. Sci. Technol. B 18, 864 (2000)
[2]E. Despiau-Pujo et al, J. Vac. Sci. Technol. A 26, 274 (2008).

5:20pm **PS-TuA12 Modeling of InP Etching under High Density Plasma of Cl_2/Ar**, *B. Liu, **A. Rhallabi**, J.P. Landesman,* Institut des Materiaux Jean Rouxel, France, *J.L. Leclercq*, Institut des Nanotechnologies de Lyon, France

It is now evident that the improvement of the optical and electrical performances of the III-V components depends on the optimization of the critical process steps such as the dry etch processes especially for the submicron devices. The simulation of plasma surface interaction may widely contribute to the optimization of such process type. In the present study, a gas phase kinetic model of Cl2/Ar plasma combined to surface model is developed to predict the etching profiles as a function of the plasma parameters. The gas phase kinetic model is based on the mass balance equations of reactive species. The kinetic constants of electron impact reactions are established as a function of electron temperature assuming maxwellian distribution of electron energy. The additional equation of power balance in the ICP reactor allows to determine the electron temperature evolution with the plasma discharge parameters (Rf power, reactor pressure and the chlorine flow rate). Parametric studies concerning the effects of the plasma parameters like power, pressure and percentage of Cl2 on the transport of charged and neutral specie evolutions have been carried out. On the other hand, the simulation results show that electron density and the dissociation rate of Cl2 are more sensitive to the surface recombination coefficient of atomic chlorine. The later is estimated at 0.15. Langmuir probe is used to measure the electrical parameters of Cl2/Ar plasma mixture such as, electron temperature and density as a function of the plasma discharge parameters. A satisfactory agreements between the simulations and the experiments have been observed One of the advantage of our model is the coupling between the plasma chemistry model and the surface etching model. The later is based on the Monte-Carlo approach which allows to describe, in a probabilistic manner, the surface mechanisms for InP etching . The direct fluxes of the reactive species such as Ar+, Cl2+, Cl+ and Cl are determined from the gas phase kinetic model and introduced as the input parameters in the InP etching model. The simulation results show the role of different plasma parameters on the etched surface profiles.

* PSTD Coburn-Winters Student Award Finalist

Plasma Science and Technology
Room: Hall D - Session PS-TuP

Plasma Science Poster Session

PS-TuP1 Steady-State and Transient Hydrocarbon Production, and Retention in a-C:D Thin Films by Low Energy Impact Atomic and Molecular Deuterium Projectiles, ***H. Zhang***, Oak Ridge National Laboratory

We report production yield of methane and heavier hydrocarbons for deuterium atomic and molecular ions incident on a-C:D thin films in the energy range 10-200 eV/D. the yields were determined at sufficient accumulated ion beam fluences that steady-state conditions were reached. In addition to steady-state chemical sputtering yields, we have studied transient hydrocarbon production, re-emission and retention of hydrocarbons from pre-loaded sample surface immediately after the start of beam irradiation. When the surfaces were prepared by irradiation to saturation with lower energy deuterium beams, transient hydrocarbon and re-emission yields significantly larger than steady-state values were observed, which exponentially decayed as function of beam fluence. The initial yield values are related to the starting hydrocarbons and deuterium densities in the prepared sample; while the exponential decay constant provide information on the hydrocarbon kinetic release and detrapping cross sections. Interestingly, this transient effect when ion bean is on can be used to determine experimentally the retention hydrocarbon concentration in amorphous deuterated carbon films after low energy ion beam impacts.

PS-TuP2 Invesitgation of Growth Mechanism of Diamond-like Carbon Film, ***M. Shinohara***, *Y. Matsuda, H. Fujiyama,* Nagasaki University, Japan, *T. Nakatani*, Toyo a-tec Co. LTD., Japan

There has been much interest in diamond-like carbon (DLC) films because they have a lot of useful properties: mechanical hardness, chemical inertness, and changeable electrical properties. Further, DLC films were deposited at low temperatures by using plasma process. The films have been used as coating materials for mechanical apparatus. On the other hand, DLC films should be used as electrical and electronic device materials, if the deposition of DLC films has to be controlled in atomic level. Therefore, it is important to understand the growth mechanism of the DLC films. Only a few papers proposed growth mechanism: the deposition rates of DLC films were decreased with the increases of the substrate temperatures; this was because the hydrogen radical generated in plasma was etched the carbon films. However there are a lot of problems left in this model. Thereby, we investigate the growth mechanism in PECVD process by using infrared spectroscopy and deposition/etching rates. We found the decrease of the deposition rates was not due to the hydrogen radical etching, but to the decreases of the adsorption coefficient of hydrocarbon radicals generated in plasma. This was because the etching rates were not increased by the increases of the substrate temperatures. We also found that the types of hydrocarbon species in the DLC films were changed by the substrate temperatures less than 300 degree C during the deposition; in this temperature region the hydrogen was not thermally desorbed from the films. It is due to the activation of the hydrogen abstraction effects by the increases of the substrate temperatures.

PS-TuP3 Impact of Combinatorial Plasma Process on the Development of Organic Low-K Dielectric Film Etching, ***C.S. Moon***, *K. Takeda,* Nagoya University, Japan, *M. Sekine, M. Hori,* Nagoya University and Japan Society of Technology Agency, *Y. Setsuhara,* Osaka University and Japan Society of Technology Agency, *M. Shiratani*, Kyushu University and Japan Society of Technology Agency

Plasma etching technology is one of technologies, which have been in charge of semiconductor device industry. As it is scaled down to several tens of nanometers, the sophisticated plasma parameter control has been indispensable to achieve the process requirements. However, up to now, it was an obvious fact that a lot of trials and errors have been carried out in the development of plasma etching process by external parameters such as input power or working pressure, since there has never been the any scientific guiding principle based on plasma science. We hereby propose the development of process map called Plasma Nano Science. However, as the enormous database is necessary to establish the process map, it is difficult by conventional unit process capable of obtaining one result by one trial. At this moment, we have newly developed the combinatorial plasma process apparatus for etching of organic low-k dielectric film, which enables to acquire many results by just one experiment. Desktop-typed combinatorial plasma apparatus was realized by capacitively coupled plasma source consisted of top electrode (13.56MHz) with the diameter of 10 mm and bottom electrode (2MHz) with that of 40 mm. Process gases of hydrogen and nitrogen were used for etching organic low-k dielectric film. Optical emission intensity of combinatorial plasma was investigated by ICCD camera and we could confirm the formation of intentional non-uniform plasma with gradient on the bottom electrode. The spatial distributions of H and N radical densities were measured by compact vacuum ultraviolet absorption spectroscopy (VUVAS) system designed and developed by our group[1] and the etching characteristics of combinatorial plasma process were interpreted by radical density. As a result, impact of combinatorial plasma process on the development of organic low-k dielectric film etching in terms of internal parameters was confirmed for the first time. The combinatorial plasma process will open a new avenue for the establishment of plasma nano science.

[1]S. Takashima, M. Hori, T. Goto, A. Kono, M. Ito and K. Yoneda, Appl. Phys. Lett. 75, 3929 (1999).

PS-TuP4 Surface Fluorination of Ultra High Molecular Weight Polyethylene using Electron Beam Generated Plasmas, ***S.G. Walton***, *E.H. Lock,* US Naval Research Laboratory, *A.A. Bujanda, D.D. Pappas*, US Army Research Laboratory

The intrinsic bulk properties of polymers make them ideally suited for light-weight, conformal protective outerware or devices. Their surfaces properties, on the other hand, require modification to realize their full potential and plasma treatment is one of the most powerful techniques to tailor the functionality of polymer surfaces. In this study, we use pulsed, electron beam generated plasmas to modify the surface of ultra high molecular weight polyethylene (UHMWPE) films. One advantage of these plasmas is the ability to regulate the ion flux and energy at the polymer surface. Under typical operation, the kinetic energies of the incident ions are at or below the energies of the polymer bonds, thus limiting damage caused by ion bombardment. The plasma-polymer interaction produces fluorine-containing groups on the surface, leaving the polymer bulk properties unaffected. Preliminary results indicate that the plasma-treated surfaces exhibit increased hydrophobicity, X-ray photoelectron spectroscopy (XPS) shows the presence of chemically bonded fluorine groups on the surface, and AFM indicates minimal changes in surface morphology. The results from these studies are used to understand the fluorination of ultra high modulus polyethylene fibers under similar plasma conditions. This work was supported by the Office of Naval Research. EHL is an NRC/NRL Postdoctoral Research Associate.

PS-TuP5 Measurement of the Isoelectric Point of Plasma Modified Surfaces and Plasma Polymerized Thin Films, *S. Pease,* ***E.R. Fisher***, Colorado State University

Plasma polymerization and plasma modification are often used to tailor the surface properties of materials. One important, but often overlooked property of materials is the isoelectric point, which is a critical measure of the acid/base properties of a variety of surfaces, most notably metal oxide surfaces. The isoelectric point for surfaces can be determined using contact angle methods as a function of the pH of the water solution used for the measurements. Here, we have treated a variety of metal oxide surfaces, including SiO_2, SiO_xN_y, and ZrO_2 with Ar plasmas to determine the effect of plasma treatment as well as aging on the isoelectric point of the surfaces. SiO_2 substrates exhibit a significant increase in isoelectric point upon treatment, from ~4.9 to ~6.0, depending on substrate location in the plasma. Upon aging, there is no change in the isoelectric point. In contrast, the SiO_xN_y substrates exhibit little change in isolectric point upon treatment, and no subsequent changes are observed upon aging. XPS compositional data will also be presented to corroborate changes in surface composition upon treatment as well as upon aging of the substrates. Additional contact angle and XPS data will be presented on plasma-deposited metal oxides (e.g. SiO_x and SiO_xC_y) and polymers (e.g. poly(allyl alcohol) and polyamides) for comparison.

PS-TuP6 Plasma Processing with CH_3OH, ***K.J. Trevino***, *E.R. Fisher*, Colorado State University

Traditional plasma processes including deposition, etching, and surface modification have been utilized in a variety of commercial applications. These applications can require highly toxic and expensive monomers; to avoid these issues, we have been exploring the use of CH_3OH for a variety of both nontraditional and traditional applications. First, the non-traditional application for plasmas of contaminated water remediation, has been explored using CH_3OH as a model compound for organic contaminants. It was chosen as a standard to compare larger organic molecules to in the future for detection and abatement with optical emission spectroscopy (OES). These studies were performed in a glass tubular reactor equipped with OES detection. Results for both CH_3OH and methyl tert-butyl ether (MTBE) contaminated water demonstrated that not only is detection of

organic molecule breakdown possible, but abatement can also be achieved. Our data demonstrate this for CH3OH and MTBE at detectable limits of 0.01 ppm. Second, data for OH radicals from our imaging of radicals interacting with surfaces (IRIS) technique will be presented for both CH_3OH and H_2O plasmas. These two simple systems allow us to understand the behavior of OH radicals from different precursors. Results from these studies will be compared to previous studies, especially with respect to how plasma parameters affect the underlying chemistry occurring in the plasma. Finally, preliminary results will be presented from studies designed to explore the use of CH_3OH plasmas as an etchant. These studies were completed in a capacitively-coupled parallel plate reactor (PPR) and include OES, scanning electron microscopy (SEM), and profilometry measurements. Comparison to traditional halogenated systems will also be presented.

PS-TuP7 Efficiency Improvement of Organic Solar Cells with Plasma Patterning and Surface Treatment, ***H. Chae****, C. Pang, K. Park, D. Jung, H. Kim*, Sungkyunkwan University, Republic of Korea

Plastic organic solar cells are getting attention due to its possible advantages in flexibility and processing costs. In this presentation, brief review of issues of plastic solar cells will be discussed with possible solutions. Our approaches to improve efficiency of plastic solar cells with plasma processing of electrodes will be discussed in details. One of the approaches is to improve the efficiency of polymer solar cells by patterning indium tin oxide (ITO) electrode layer. Light absorbance was enhanced with ITO layer patterning for the improvement of power conversion efficiency of polymer solar cells. The line-and-space pattern of polystyrene layer is formed on the top of 100nm thick indium tin oxide layer by capillary force lithography process and the patterning. And surface roughening of the ITO layer were completed with O2 and Ar plasma etching with various step heights of 20nm to 60nm. We have shown that the patterning of the ITO can increase the efficiency of the plastic solar cells. Another approach to be discussed is plasma surface modification of the solar cell electrodes. Plasma processing of the ITO surface with fluorocarbon plasmas and oxygen plasma increased the efficiency of the plastic solar cells by removing organic contaminants in the ITO surface and by surface oxidation.

PS-TuP8 Polymer Modification by Electron Beam Generated Plasma in Argon, Oxygen and Nitrogen Environments and Their Mixtures, ***E.H. Lock****, S.G. Walton*, Naval Research Laboratory

The electron beam generated plasmas are efficient at generating high density plasmas over the volume of the beam, resulting in large fluxes of low-energy ions (< 5 eV) at surfaces located adjacent to the electron beam. Thus, the ion energy applied to the surface is comparable with the bond strengths found in most polymers, so it is sufficient to invoke chemical surface modification with limited morphology changes. In this study, polymer modifications resulting from electron beam plasma generation in argon, oxygen and nitrogen environments and their mixtures are investigated. The polymers of interest include polystyrene, polymethylmetacrylate and ultra-high molecular weight polyethylene. The effects of the plasma process parameters including treatment time and duty factor, as well as mixture composition on surface energy, chemistry and morphology are investigated.

PS-TuP9 Synthesis of Polyethyleneglycol and Polystyrene-Like Films by Atmospheric and Low Pressure Plasmas, *D. Merche,* ***B. Nisol****,* Universite Libre de Bruxelles, Belgium*, C. Poleunis, P. Bertrand,* Universite Catholique de Louvain, Belgium*, F. Reniers*, Universite Libre de Bruxelles, Belgium

The deposition and characterization of polystyrene (PS)-like and polyethyleneglycol (PEG)-like on a variety of substrates was investigated using “plasma enhanced chemical vapour deposition” (PECVD) under atmospheric pressure. For both PS and PEG-like deposits, an atmospheric RF plasma torch (Atomflo® 250C SurfX) was used, which consists of two closely metallic electrodes that are perforated to allow the process gas (Ar) to flow through. The precursors (styrene vapour or tetraglyme droplets) were introduced into the plasma downstream to the electrodes (remote plasma). Thin films of polystyrene were also synthesized in a home-built dielectric barrier discharge (DBD), in remote and direct HF plasma. Precursor vapours (styrene) are carried out by Ar or He. PEG-like films are also obtained at low pressure, in a capacitively coupled RF discharge obtained in a cylindrical Pyrex system. PEG-like films are known for their non-fouling property, which is an important feature for many biomedical applications. XPS and SSIMS were useful in order to ensure that the precursor for PEG like films are not too strongly fragmented by plasma treatment, in which case the protein-repelling property of the samples would be compromised. XPS permits to determine the C/O of PEG-like. The non-fouling properties of those samples have been studied with Bovine Serum Albumin (BSA) adsorption. XPS was used to track the presence of proteins on the surface by using the N1s signal coming out from the protein. pp-PS films deposited on PTFE were characterized by XPS. Spectra show a significant change in C1s energy value (towards lower binding energies) in comparison with untreated PTFE. We can also observe an important amount of oxygen, indicating a strong oxygen functionnalization into the film. Consequently, the pp-PS are more hydrophilic (water contact angle) in comparison to conventional PS. The influences of the parameters and the plasma source on the FTIR spectra (IRRAS) of plasma polymers deposited on steel (pp-PS) and on gold surface (PEG-like) was investigated. FTIR on pp-PS shows a decrease of the aromaticity, and that the films are branched, cross-linked and contain hydroxyl groups. The morphology of pp-PS films were evaluated by optical microscopy.

PS-TuP10 Surface Reactions of the Surfaces of CoFeB Films Etched in High Density Cl_2/Ar Plasma, ***D.-P. Kim****, D.-S. Um, C.I. Kim*, Chung-Ang University, Korea

Magnetic random access memory (MRAM) has been developed for nonvolatile memory applications. MRAM does not need power for data-retention and relatively high speed for writing and read cycles. In addition, standby power for MRAM is low because the array leakage current is zero. MRAM consists of multi layered structure with diamagnetic/magnetic films. In order to produce high density MRAM, various structures can be achieved with using CMOS technology. Among front–end CMOS processes, the key technology to obtain high density MRAM is the etching process. The pattern transfer with smaller dimensions should be developed and optimized with using plasma etching process. Until now, the etching properties of CoFeB films in high density plasmas have not been well understood. The etch experiment were performed with using ion milling, RIE, ICP and ECR plasma. Ion milling sowed some problems such as re-deposition and low selectivity for small feature size of magnetic films. RIE etching process showed the problem of non-volatile etch by-products. The etch rates of CoFeB, CoSm, CoZr and FeMn in Cl_2 based chemistry, ICl and IBr chemistries were only reported. In Cl_2 based plasma, the highest etch rate obtained at 10% Cl_2 mixing ratio, but, the highest etch rates were can be obtained at higher ICl and IBr mixing ratio in IBr and ICl plasmas. However, they did not report the variation of components of CoFeB after etching process. In this study, CoFeB films were etched with using high density plasma system and Cl_2-based gas chemistries. Etch rate and selectivity of the CoFeB was systemically studied by the process parameters including gas mixing ratio Cl_2/Ar, RF power, DC-bias power, substrate temperature. The optical emission spectroscopy, Langmuir probe were used to monitor the behaviors of temperatures of electron and ion, energy of ion and radicals and volume densities for radicals. The etch rate of CoFeB were measured with using surface profiler. The etch rate behavior of CoFeB showed high dependent on the gas chemistry, RF power and DC bias voltage and pressure due to non-volatile etch by products. X-ray photoelectron spectroscopy analysis was used to confirm the etch rate behavior by evaluating the changes of atomic component from the surface of CoFeB after etching process. In addition, atomic force microscopy and scanning electron microscopy was investigated the changes of topology to confirm accumulation of etch by products.

PS-TuP11 Dry Etching Properties of TiN for Metal/High-k Gate Stack by using BCl_3-based Inductively Coupled Plasma, ***C.-I. Lee****,* Ansan College of Technology, Korea*, D.-S. Um, D.-P. Kim, G.-H. Kim, J.-C. Woo, C.I. Kim*, Chung-Ang University, Korea

Transistor has been scaled down since they were introducing, continually. However, it is accompanied with several problems like direct tunneling through the gate dioxide layer and low conductivity characteristic of poly-Si gate in nano-region. To cover these faults, study of new materials is urgently needed. This can be achieved by using an insulator that has a high dielectric constant. Recently, high dielectric materials like Al_2O_3, ZrO2, and $HfO_2$2 are being studied for equivalent oxide thickness (EOT). However, poly-Si gate is not compatible with high-k materials for gate-insulator. Poly Si gate with high-k material has some problems such as gate depletion and dopant penetration problems. Therefore, new gate structure or materials that are compatible with high-k materials are also needed. TiN for metal/high-k gate stack is conductive enough to allow a good electrical connection and compatible with high-k materials. So, it is a good barrier-layer material for interconnection. According to this trend, the study on dry etching of TiN for metal/high-k gate stack is needed. In this study, the investigations of the TiN etching characteristics were carried out using the inductively coupled BCl_3-based plasma system and adding O_2, Ne, and N_2. Dry etching of the TiN was studied by varying the etching parameters including BCl_3/Ar gas mixing ratio, RF power, DC-bias voltage to substrate, substrate temperature and gas addition. The plasmas were characterized by optical emission spectroscopy analysis and quadrupole mass spectrometer measurements. The chemical reaction on the surface of the etched TiN was investigated with X-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

PS-TuP12 Dry Etching of CoFeB Films using BCl_3-based Inductively Coupled Plasma for MRAM Application, ***D.-S. Um****, D.-P. Kim,* Chung-Ang University, Korea*, S.K. Lee, T.W. Jung,* Hynix Semiconductor Inc., Korea*, C.I. Kim*, Chung-Ang University, Korea

We have been in the personal computing age, but person and computer are harmonized uneasily with each other. Now, however, it is within the range of possibility. Recently many researchers are studying about ubiquitious that can provide users to access computers at anytime and everywhere. If we could make devices of smaller size, higher speed and lower power consumption, it can be realized. Magnetic RAM(MRAM) using tunnel junction is the device which can meet this requirement. Tunnel junction is consisted of two ferromagnetic layers separated by an insulator. One of the ferromagnetic layers is pinned-layer that fixed magnetization, whereas the other ferromagnetic layer is free-layer unfixed magnetization. Due to spin dependent electron tunneling one can thus have two distinct resistance states, associated with the magnetizations of the pinned and free layers parallel or anti-parallel. To improve device performance, one continuously aims to achieve higher tunnel magnetoresistance (TMR), better thermal stability and low ferromagnetic coupling between pinned and free layers. The use of amorphous CoFeB films in the free and pinned layers of optimized tunnel junctions enabled us to obtain a higher TMR coefficient, good transport properties upon annealing and lower coupling fields. Up to now, there are few papers on the plasma etching of CoFeB films using high density plasmas. However, those papers did not show the changes of component on the etched surface of CoFeB. In this study, CoFeB films were etched with using the inductively coupled plasma system and BCl_3-based gas chemistries. Etch rate and selectivity of the CoFeB was systemically studied by the process parameters including BCl_3/Ar gas mixing ratio, RF power, DC-bias power, substrate temperature. The changes of electron temperature, ion energy and radical volume densities were characterized by optical emission spectroscopy analysis, Langmuir prove and quadrupole mass spectrometer. The etch rate of CoFeB showed highly dependency on the DC bias voltage and pressure due to effective removal of etch byproducts from the exposed CoFeB surface in plasma by sputtering de-sorption. The changes of components on the surface of CoFeB were investigated with X-ray photoelectron spectroscopy. The variation of surface was also investigated with atomic force microscopy and scanning electron microscopy.

PS-TuP13 Temperature Dependence on Dry Etching of Al_2O_3 Thin Films in BCl_3/Cl_2/Ar Plasma, ***X. Yang****, D.-P. Kim, D.-S. Um, C.I. Kim*, Chung-Ang University, Korea

High-κ gate dielectrics and metal gate electrodes are required for enabling continued equivalent gate oxide thickness scaling, and hence high performance, and for controlling gate oxide leakage for both future silicon and emerging non-silicon nanoelectronic transistors. Significant progress has been achieved in terms of the screening and selection of high-κ insulators, understanding their material and electrical properties, and their integration into CMOS technology. During the etching process, the wafer surface temperature is an important parameter which influences the reaction probabilities of incident species, the vapor pressure of etch products, and the re-deposition of reaction products on feature surfaces. It mainly depends on the chuck temperature, the ion density and ion energy and the exothermicity of the etching reaction. In order to obtain the good etching environment, sudden changes of temperature in the plasma condition during the transition between processes steps should be well controlled .In addition, the true substrate temperature is difficult to monitor. For this reason, the experiment according to the substrate temperature change was progressed. In this study, we investigated that the effect of substrate temperature on the etch rates and selectivity of Al_2O_3 over Si and hard mask materials (such as SiO_2, and Si_3N_4) thin film in inductively coupled plasma in function of (BCl_3/Ar)+ Cl_2 gas mixture ratio, RF power, DC bias and chamber pressure base on the substrate temperature increases from 10 °C to 80 °C,. The chemical reactions on the etched surface were investigated with using x-ray photoelectron spectroscopy. The morphology changes of exposed surface in plasma were investigated with atomic force microscopy. The etch profile was evaluated with SEM as functions of parameters.

PS-TuP14 Aspect Ratio Dependent Twisting and Mask Effects During Plasma Etching of SiO_2 in Fluorocarbon Gas Mixtures*, ***M. Wang****, M.J. Kushner*, Iowa State University

During plasma etching of via-like structures having high aspect ratios (HAR > 10), twisting is sporadically observed. This is where an otherwise straight feature will turn from the vertical. Twisting may occur in only a few percent of features among other features that have unaltered profiles. The effect is most frequent when feature size openings to the plasma are only tens of nm. Twisting in plasma etching of SiO_2 has been computationally investigated using the Hybrid Plasma Equipment Model to obtain the energy and angle distribution of ions and neutrals; and the Monte Carlo Feature Profile Model to predict profiles. The basic operating conditions are a capacitively coupled plasma sustained in $Ar/C_4F_8/O_2$ = 80/15/5 (1 kW, 10 MHz, 40 mTorr, 300 sccm). Parametric investigations were made while varying aspect ratio (10-40), height of the photoresist mask, power deposition and reaction probabilities (e.g., angular dependence of scattering). When including charging, features should be resolved with atomic-scale resolution to eliminate numerical effects. We found that as the feature size decreases, the flux entering the feature becomes more stochastic in nature. This randomness in the flux can then lead to variations in both the total etch rate on a feature-to-feature basis as well as on the profile. For example, preferential polymer buildup on one side of the feature may produce asymmetric etching. These effects are magnified when including charging as the stochastic nature of the flux produces errant local electric fields that deflect ion trajectories. The height and character of the mask material potentially has an important role in twisting. The photoresist height contributes to the effective aspect ratio; and its electron and ion scattering characteristics contribute to deliver of charge deeper into the feature.

*Work supported by the Semiconductor Research Corp., Micron Inc. and Tokyo Electron Ltd.

PS-TuP15 The Analysis of ZrO_2 Thin Films Etching in BCl_3/Cl_2 Inductively Coupled Plasma, ***H.-J. Kim****, D.-P. Kim, G.H. Kim, J.-C. Woo, D.-S. Um,* Chung-Ang University, Korea*, C.-I. Lee,* Ansan College of Technology, Korea*, C.I. Kim*, Chung-Ang University, Korea

As feature size of CMOS device has been decreased 100 nm, the new material has required to substitute for SiO_2 as gate dielectric material. The silicon oxide for gate reached a physical limit owing to very high gate leakage current of 10 A/cm^2 for very thin gate SiO_2 of below 1nm. Therefore, high dielectric constant materials, such as HfO_2, ZrO_2, and Al2O3 have attracted a great attention. Among them, ZrO_2 is the most candidate because of its high dielectric constant of 20 ~ 25, wide bandgap of 5~7 eV, and thermal stability with Si. In order to obtain a small feature accurate pattern transfer, development of plasma etching process for ZrO_2 thin film is important problem to be solved. There are few papers on the etch of ZrO_2 thin films with using helical resonator plasma and electron cyclotron plasma in Cl_2/BCl_3. They reported that etch rate of ZrO_2 is limited by the low volatile etch by product such as $ZrCl_2$, but the etch rate can be accelerated by the addition BCl_3 which can be effectively remove oxygen from the surface of ZrO_2. However, there is no relationships between input parameters and plasma chemistry as well as surface reactions. In present work, the etching characteristics of ZrO_2 thin film was investigated with using inductively coupled BCl_3/Cl_2 plasma. ZrO_2 thin film was deposited on Si substrate by atomic layer deposition (ALD). The variation of etch rate and selectivity was monitored while additive gases was varied in BCl_3/Cl_2 plasma. Simultaneously, the etch behavior of ZrO_2 was investigated with variation of RF power, DC bias voltage, and pressure. To understand the influence of additive O_2, He or N_2 into BCl_3/Cl_2 on the electron temperature and the density of radicals, Langmuir probe (LP), optical emission spectroscopy (OES), quadrupole mass spectromter (QMS) was used during etching process.

PS-TuP16 Effective Measurements of Plasma Process-Induced Damage Related to Dielectric Integrity Degradation on Gate Oxide using Practical Structure, ***J. Lee****, H. Lee, H. Kim,* Samsung Electronics, Korea*, I.S. Chung*, Sungkyunkwan University, Korea

Monitoring techniques are required to understand the root cause of the damage and how to optimize the process or equipment. Many techniques for plasma damage monitor were introduced.[1,2] But it was difficult for them to identify the plasma process-induced damage because of unrealistic and complicated structures. Therefore, the plasma process was optimized and verified with newly-designed test structure to monitor wafers. The presented structure based on an unconventional antenna structure is very simple but effective to measure the plasma charging damage, which correlates to real circuit performance, such as parametric shifts, hot carrier response, and dielectric integrity degradation[3]. It was composed of various antenna ratios, active areas, and patterned features for detecting electron shading effect, plasma non-uniformity and ion bombardment damage. Electrical tests including threshold voltage shift, hot carrier stress, and breakdown voltage have been performed to detect plasma damage.

[1] An Efficient Method For Plasma-Charging Damage Measurement, K. P. Cheung, IEEE ELECTRON DEVICE LETTERS, 11(1994)460.

[2] A Test Structure for Plasma Process Charging Monitor in Advanced CMOS Technologies, Sang U. Kim, IEEE, (1997) 57.

[3] Plasma damage in thin gate MOS dielectrics and its effect on device characteristics and reliability, Tomasz Bro_zek, Microelectronics Reliability, 40(2000)625

PS-TuP17 Reaction Mechanisms and Profile Evolution for HfO_2 High-K Gate-stack Etching: Integrated Reactor and Feature Scale Modeling*, ***J. Shoeb****, M.J. Kushner*, Iowa State University

To minimize leakage currents resulting from the thinning of the insulator of the gate-stack of field effect transistors, high-k metal oxides, and HfO_2 in particular, are being implemented as a replacement for SiO_2. To speed the

rate of processing, it is desirable to etch the gate stack (e.g., metal gate, anti-reflection layers, dielectric) in a single process while having selectivity to the underlying Si. Plasma etching using $Ar/BCl_3/Cl_2$ mixtures have been shown to effectively etch HfO_2 while having a good selectivity with respect to Si. In this talk, we discuss results from integrated reactor and feature scale modeling of gate stack etching in chlorine plasmas. The stack consists of an erodible photoresist mask, metal gate and HfO_2 with underlying Si (and possibly anti-reflection layers). Reactant fluxes were obtained from reactor scale modeling of inductively and capacitively coupled plasma tools using the Hybrid Plasma Equipment Model. Surface reaction mechanisms were developed using its Surface Kinetics Module. The mechanisms were implemented in the Monte Carlo Feature Profile Model with which etch profiles are predicted. We found that BCl_x species produced by electron impact in the plasma react with HfO_2 which, under ion impact, form volatile etch products such as B_xOCl_y and $HfCl_x$. Selectivity to Si is achieved by boron creating Si-B bonding as a precursor to the deposition of BCl_x polymer, which slows the etch rate relative to HfO_2. The low ion energies required to achieve this selectivity then challenge one to obtain highly anisotropic profiles in the metal gate portion of the stack. Validation was performed with data from the literature. Results will be discussed from parametric studies of process variables (e.g., gas mixture, power, bias) on etch rate and profile.

*Work supported by the Semiconductor Research Corp.

PS-TuP18 A Reduced Model for Etch Rate Prediction Based on Plasma Parameters, ***M. Klick**, L. Eichhorn, R. Rothe*, Plasmetrex GmbH, Germany

The virtual metrology is the prediction of plasma etch rates and critical dimensions is based on measurements of pre-process values and plasma parameters. This can be realized by a self-consistent model of plasma and process or non- self-consistent (empirical) model with plasma parameters measured in real-time and in situ. A self-consistent plasma model must describe the complete plasma process. Already the real-time solution for a self-consistent plasma model is impossible, in particular due to large amount of also chemical mechanisms. The effort can be reduced dramatically by usage of plasma parameters, describing the main physical and chemical mechanisms. The most important issue of development of a chemical / physical model is to identify the key parameters. Tool parameters reflect only the tool properties but not the real process. The most important process parameters, called key parameters, are plasma density and electron collision rate by SEERS (physics), RF-parameters by VI-probe, radical/polymer concentrations by OES (chemistry). Our reduced approach for reactive ion etching as described above assume a combination of a physical (sputter) effect, a pure chemical (surface) reaction, and a physical-chemical mechanism. Despite the pressure is usually kept constant, the real important parameter is the density of the gas (neutrals) which depends on the temperature additionally. The gas temperature is usually not available but replaced here by the electron collision rate which is proportional to the gas density and so reciprocally proportional to the gas temperature. The model was applied to oxide etch with F-chemistry, the unknown coefficients were determined and prediction error was shown to be less than 5%.

PS-TuP19 Molecular Dynamics Simulation of Si Etching by Monoenergetic Br^+, Br_2^+, H^+, and HBr^+ Ions Generated in HBr Plasmas, ***T. Nagaoka**, H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Dry processing technology with chemically reactive plasmas has been widely utilized for the fabrication of semiconductor devices. At present, HBr plasmas are standard for Si etching processes (e.g., gate etch and shallow trench isolation etch in the fabrication of SRAM). Here we first report molecular dynamics (MD) simulation of Si etching by HBr or Br_2 plasmas. The Simulation procedure is as follows. In the 3D simulation cell (cross section=3.2^2 nm^2, depth = about 5 nm), about 1,500 silicon atoms are initially located in the structure of diamond lattice. Atoms in the bottom layer are fixed and periodical boundaries are imposed in the horizontal direction. To this Si(100) substrate, 20-300 eV ions are impinged in the direction normal to the surface. In this study, we used an improved Stillinger-Weber interatomic model partially including multibody interaction. Parameter sets for Si/H/Br were newly determined based on ab-initio data. We focused on monochromatic beam etching by Br^+ (Cl^+), Br_2^+ (Cl_2^+), H^+, and HBr^+ ions without radicals. First, we confirmed the different etching characteristics between cases of Br and Cl. Yields by Br^+ and Br_2^+ were lower than those by Cl^+ and Cl_2^+ at the same ion energy. This tendency agrees with experimental results.[1] Additionally, yields by diatomic ions were higher than those by monatomic ions. The energy dependence of etch yield will be presented. Secondly, we estimated the halogen coverage. The Br coverage for Br^+ impact was lower than Cl coverage for Cl^+ impact. For the case of Br^+ with an ion energy of 50 eV, the depth of reaction layer and Br coverage were about 20 Å and 7.7×10^{14} cm^{-2}, respectively. On the other hand, for Cl^+ impact, the depth of the reaction layer and Cl coverage were about 30 Å and 1.7×10^{15} cm^{-2}, respectively. These coverages are in good agreement with experimental results of 6.0×10^{14} cm^{-2} and 1.0×10^{15} cm^{-2} using HBr and Cl_2 plasmas, respectively, where a dc bias voltage is -35V.[2] In this conference, the effect of H^+ on etching mechanisms will be also discussed.

[1]S. A. Vitale et al., J. Vac. Sci. Technol. A 19,2197 (2001).

[2] C. C. Cheng et al, J. Vac. Sci. technol. A 13,1970 (1995).

PS-TuP20 A Novel Interatomic Potential Model for MD Simulation of Si Etching by Cl^+/Br^+ Containing Plasmas, ***H. Ohta**, T. Nagaoka, K. Eriguchi, K. Ono*, Kyoto University, Japan

Plasma-surface interaction is an important research subject both academically and industrially. Particularly, the understanding of interaction between chemically reactive plasmas and semiconductors is inevitable for further improvement in the fabrication of semiconductor devices. At present, HBr plasmas are utilized for state-of-the-art fine Si etching processes. However, fundamental experimental data were not sufficient except for some plasma experiments.[1] In addition, potential models for Si/F and Si/Cl systems were only available for Si etching simulations. Here we present an novel interatomic potential models to realize classical molecular dynamics (MD) simulation of Si etching by HBr plasmas. Our simulation target is Si etching by HBr or Cl_2 plasmas. First, the scheme to construct potential function was renewed, where all parameters could be systematically determined based on ab-initio data obtained from quantum chemical calculation. As a potential form, we selected the well-known Stillinger-Weber (SW) model, where the total potential is expressed by the sum of two- and three-body functions. SW model could reproduce ab-initio data with high accuracy when systems include only two or three atoms. Secondly, a new discipline to construct potential model is also proposed. We clarified how the potential functions affect etching characteristics in MD simulations.[2] Until now, SW potential models for etching simulation were determined on the basis of potential energies calculated for small clusters while the energies for ion penetration and stay in interstitial sites have not been considered. However, the latter crucially affects the results of etching simulation, especially the morphology of the reaction layer. Then, the accurate estimation of potential energies for ion penetration in interstitial sites is essential for qualitative improvement of etching simulations. After careful examination, it was founded this energy was overestimated when the original SW model was used. Based on this fact, we proposed an improved SW model, where a new term is added to three-body potentials. In this conference, we present a detail derivation of the new model and the comparison between results by old and new SW models.

[1]e.g., S. A. Vitale et al., J. Vac. Sci. Technol. A 19, 2197 (2001).; C. C. Cheng et al., J. Vac. Sci. Technol. A 13, 1970 (1995).

[2]A. Iwakawa et al., to be published in Jpn. J. Appl. Phys.

PS-TuP21 Numerical Simulations for a Radio-Frequency Micro-Atmospheric Pressure Plasma Jet and Coupling with Laser Diagnostics, *J. Waskoenig, **K. Niemi**, T. Gans*, Queen's University Belfast, Northern Ireland

Atmospheric pressure plasmas in particular micro-discharge devices have tremendous application potential and are already used and targeted for a variety of technological and bio-medical applications. Micro-atmospheric pressure plasma jets (μ-APPJs) can provide high concentrations of radicals at a low gas temperature, particularly for modification of sensitive surfaces, such as in biomedicine or for surface coatings. Nevertheless the fundamentals of these non-equilibrium plasmas at ambient pressure are only rudimentarily understood. In general, the diagnostics of atmospheric pressure plasmas is extremely challenging, therefore numerical simulations offer a further insight into these discharges. The presented 1D-model is a numerical fluid-model along/across the discharge gap for a μ-APPJ. Dual frequency (2f) excitation of the μ-APPJ promises enhanced efficiency concerning the radical production and additional control for the plasma production. The discharge dynamics of the 2f excitation is investigated in various parameter ranges. Modelling and numerical simulations are however mainly restricted due to the lack of available data, particularly for surface processes which are crucial at these small dimensions because of the extraordinary high surface to volume ratios. Using experimentally measurable quantities as fixed input parameters of the model offers the opportunity to overcome this lack of available data. The μ-APPJ has been specially designed to provide an excellent optical diagnostic access to the discharge volume. Absolute atomic radical densities can be measured using two-photon absorption laser-induced fluorescence spectroscopy for use as a fixed input parameter in the model. Absolute measurements require detailed knowledge of collisonless de-excitation processes in particular under atmospheric pressure conditions. This can be obtained from the effective fluorescence decay rate (estimated lifetime of about 100 ps). The required temporal resolution can be achieved using a tuneable UV Fourier-limited picosecond laser system (1 cm^{-1}, 10 ps). Within the simulation the sticking

coefficient for atomic oxygen loss at the electrode surfaces is varied until consistency with the locally measured atomic oxygen ground state density is reached.

PS-TuP22 A Comprehensive 3D Fully Coupled Model of a Gas Discharge for the Simulation of Magnetron Sputtering Systems, ***F.J. Jimenez,*** University of Alberta, Canada*, D. Field,* NuCryst Pharmaceuticals, Canada*, S. Ekpe, S.K. Dew*, University of Alberta, Canada

Sputter deposition is a well established technique underlying a wide range of technological applications. However, the system is complex, involving coupled interactions of plasma, target, transport and substrate. Several models have been developed to explain and to optimize the process conditions. Nevertheless, the majority of these models excluded or simplify some key parameters missing the benefits that may arise using a detailed model. We present a comprehensive 3D coupled model where each part of the process is isolated in modules. Transport of charged and neutral particles is solved using a hybrid algorithm where energetic particles are followed individually using a Direct Monte Carlo (DMC) approach and thermalized particle transport is described by a computational fluid dynamics model modified to account for the nonuniform magnetic field. The plasma model is solved self-consistently using an octree grid with local refinement in the region next to the cathode to resolve the thin sheath typical of magnetron sputter systems. The highly coupled system of partial differential equations is numerically solved using a modified Newton method. An iterative approach is used to surmount the coupling arising between the glow discharge and the rarefaction and heating of the background gas. For experimental verification, a planar magnetron with an Aluminum target has been used as the reference system. The discharge has been characterized using a custom Langmuir probe. Plasma densities are shown to increase with power and pressure as would be expected. Electron temperature on the other hand decreases with pressure and power for the process conditions studied (5-40 mTorr, 75-300 W). At high pressures and/or high powers, the rate of reduction in electron temperature decreases, suggesting the effect of process gas rarefaction. At these pressures and powers significant rarefaction has been observed indicating a trend between this effect and plasma parameters. This may suggest a more decisive role of the gas-plasma interaction when modeling magnetron sputtering systems in this pressure regime.

PS-TuP23 Kinetic Simulations of Dielectric Facing Plasma and Sheath under Application of Microwave Energy, ***D. Smithe,*** Tech-X Corporation*, R. Bravenec,* Tokyo Electron America, Inc.*, P. Stoltz, C. Roark,* Tech-X Corporation*, M. Funk, L. Chen,* Tokyo Electron America, Inc.*, E. Kase*, Tech-X Corporation

Generation and heating of plasmas by microwaves to an overdense state ($\omega<\omega_{pe}$), where the waves should be cut off, is not completely understood. We study sheath formation and behavior at the interface between an insulating dielectric and an un-magnetized plasma, using electromagnetic particle-in-cell simulation techniques.[1] Various scenarios are of interest here, including both situations in which the plasma is under-dense and over-dense, or transitions from under-dense to over-dense. In the case of over-dense plasma, we look at situations involving incident electromagnetic radiation resulting in field components both parallel and perpendicular to the plasma interface, and are interested in the skin-depth penetration of the waves into the plasma. Of particular interest is the resonance of the EM waves at the location in the sheath where the wave frequency matches the plasma frequency and can serve as the major source of heating of over-dense plasmas[2] The simulations include the effects of ionization, and allow us to study the buildup of plasma density associated with ionization in the presence of the large fields of the RF-enhanced sheath. The ionization model is a Monte-Carlo type model, with energy dependant cross-section.[3] We are also studying the effects of secondary emission processes from the dielectric interface. For example, copious secondary emission is seen to reduce or even momentarily reverse the sign of the sheath. Our secondary emission model[4] was originally designed for metallic emission surfaces, but it being re-engineered to treat secondary emission from dielectric materials. It allows for energy and incident angle dependant yield, and produces a specific energy spectrum of outgoing particles. The overall goal of this work is to develop an analytical or tabular model of the sheath for use in fluid models of plasma.

[1] "VORPAL: a versatile plasma simulation code," C. Nieter and J. R. Cary, J. Comp. Phys., vol. 196, pp. 448–472, 2004.

[2] "High energy electron generation in surface-wave-produced plasmas," Yu M. Aliev, V. Yu Bychenkov, A. V. Maximov, and H. Schluter, Plasma Sources Sci. Tech. 1 (1992) pp. 126-131.

[3] Theory and Design of Charged Particle Beams, Martin Reiser, Wiley, New York, 1994.

[4] "Probabilistic model for the simulation of secondary electron emission," M. A. Furman and M. T. F. Pivi, Phys. Rev. ST Accel. Beams 5 (2002).

PS-TuP24 Effects of Etching-Mask Geometry and Charging on Etching Profile Evolution, ***H. Fukumoto****, H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Two-dimensional etching profile evolution in two different geometries, an axisymmetric hole and an infinitely long trench, has been calculated to clear effects of etching-mask geometry and charging on etching profile evolution. In the simulation, SiO_2 etching by fluorocarbon plasmas is assumed because of widely employed processes for the fabrication of contact and via holes in the SiO_2 film. The model takes into account the transport of particles in microstructures, together with surface reactions therein through sputtering, ion-assisted etching, chemical etching, and deposition. The model includes ions and neutrals (CF_x^+, CF_x, F; x=1-3) coming from the plasma, under different conditions of particle temperature, density, and ion energy. The neutral particles from the plasma onto substrate surfaces are assumed to travel in microstructures with diffusive reflections on feature surfaces, while the ions accelerated through the sheath on the substrate travel with specular reflections on feature surfaces. The cell removal method is employed to represent the feature profile evolution, where the SiO_2 is represented by two-dimensional discrete cells. Numerical results indicate that the etching profiles of hole and trench have the similar tendency under varying input parameters such as plasma species densities, ion energy, and mask aspect ratio. However, the etching-mask geometry shows some differences in the two structures; the resulting profile is narrower and shallower in the hole than in the trench, where the incident neutral fluxes are more reduced in the hole. Moreover, the profile of the trench has lateral etches such as undercut and bowing on sidewalls. The velocity distribution of neutral particles contributes to the difference of the etching profile evolution in the two structures; in effect, the velocity distributions are the more isotropic in the trench, because less neutral particles interact with mask sidewalls in the trench. Thus, it follows that geometrical structures contribute significantly to the behavior of neutral particles therein, and characterize the resulting etched profiles. The etching-mask geometry and the SiO_2-etched feature also make the differences in charging potential at the feature bottom in the trench being lower than in the hole, because the trench feature surface obtains more electron flux owing to its geometrically smaller shadowing effect.

PS-TuP25 Plasma Surface Texturing of Metals, ***E. Park****, K. Casey, M. Morud, K. Taylor*, Medtronic, Inc.

A novel plasma process for creating a nanometer and micron-scale textures on MP35N alloy surfaces using radio-frequency (RF) inert gas plasmas was investigated, with a focus on characterizing the relationship between process variables and the resulting microstructure. This unique plasma texturing technology provides several advantages over other coating-based texturing processes. Because it is a surface modification process, coating delamination and loose particulates, which would cause serious problems in biomedical applications, are not of concern. Possible applications of the textured surfaces include drug reservoirs, surfaces that promote tissue or bone in-growth, and any applications benefited by high surface areas. In the plasma texturing process, metal samples were placed directly on the substrate holder that was electrically connected to an RF electrode. Typical process parameters for Ar plasma texturing included 200W to 800W of power, pressures of 20 mTorr to 80 mTorr, and process times of 8 min to 10 min. A variety of surface textures with differently sized features have been formed varying from individual pillars to three dimensional, interconnected porous structures. The microstructures that evolve were believed to result from the loss of material from the metal sample, due to the combination of interactions of Ar ions with the sample and subsequent heating of the metal surfaces. The amount of material removed from MP35N alloy samples during texturing ranged from 4 to 10 % of the initial mass of the sample depending on the degree of texturing. Process variables, including RF energy and pressure, as well as properties of the material to be textured (thermal and electrical transport properties and sample geometry) were all found to affect the degree of texturing and type of microstructure formed. To create surfaces with more complex textures, the plasma textured surface has been modified by subsequent surface treatments and depositions. This secondary process can form additional microstructures on the already textured surface or modify surface chemistry and properties.

Plasma Science and Technology
Room: 304 - Session PS1-WeM

Plasma-Surface Interactions in Materials Processing I
Moderator: S. Agarwal, Colorado School of Mines, L. Stafford, Universite de Montreal, Canada

8:00am **PS1-WeM1 Studying the Interaction of Atomic Hydrogen with a-Si:H Thin Films using Evanescent-Wave Cavity Ring-Down Spectroscopy**, *F.J.J. Peeters,* ***J. Zheng****, I.M.P. Aarts, A.C.R. Pipino, W.M.M. Kessels, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) is applied to an a-Si:H thin film subjected to quantified H fluxes from an atomic H source in the range of $(0.4\text{-}2)\times10^{14}$ $cm^{-2}s^{-1}$. To this end a ~40 nm a-Si:H film was grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by thermal decomposition of silane on a hot filament. The observed changes in the optical loss during H dosing are attributed to the creation and healing of sub-gap Dangling Bond (DB) defect states and were measured with a sensitivity of $\sim10^{-6}$ and a time resolution of 33 ms. The DB density is shown to increase during H dosing cycles and the DBs reversibly 'heal' when the H flux is terminated. The effect increases in magnitude with H flux and approaches saturation at the highest attainable flux of 2×10^{14} $cm^{-2}s^{-1}$. Initial rates for both uptake and healing are linear with flux. Through the use of polarizing optics the CRDS signal was split into s- and p-polarized components, which, combined with field calculations, revealed that H-induced DB formation is not limited to the surface of the film but progresses into the bulk with a penetration depth of ~10 nm. The steady-state penetration depth appears to be independent of flux within the range of our experiment. A similar process is observed for defect creation during growth of the film. Extensive kinetic modeling of the observed behavior is used to understand the hydrogen-material interactions and DB formation in a-Si, which are of key importance in a-Si:H thin film solar cells.

8:20am **PS1-WeM2 Unraveling the Importance of the Bimodal Energy Distribution of Bombarding Ions in Fluorocarbon Plasma Etching**, ***F.L. Buzzi****, Y.H. Ting, A.E. Wendt*, University of Wisconsin-Madison

Ion bombardment provides a key benefit in plasma etching for microelectronics fabrication and other materials processing applications. A sheath electric field accelerates ions into the substrate so they strike at normal incidence, contributing energy and reactive species to enable anisotropic etch profiles. The energy of the bombarding ions is a significant parameter, and is typically controlled coarsely by adjusting the time-averaged sheath voltage through the application of a sinusoidal bias voltage to the substrate electrode. The sinusoidal voltage waveform produces a broad “bimodal” ion energy distribution (IED) at the substrate, with two ion flux maxima, at respective energies considerably above and below the average. In order to deconvolve the effect of ions of multiple energies bombarding the substrate simultaneously, we have manipulated the waveform of the bias voltage to produce two ion flux maxima. By systematically tailoring the shape of the waveform, the energies and relative fluxes of the two IED peaks are varied independently over a 100 to 500 eV range in a fluorocarbon-based helicon plasma, while silicon dioxide and photoresist etch rates are monitored. Fluorocarbon plasmas create a competition between deposition and etching on the substrate surface, so that with a single IED peak at 100 eV, net deposition is observed, while etching with a monotonically increasing etch rate is observed for a single peak in the 200 to 500 eV range. Two experiments were conducted in which a 100 eV IED peak was combined with a higher energy peak, varying the energy and relative flux of the high energy peak, respectively. In both cases, a relatively small contribution of high energy ions clearly leads to considerable etch rate enhancement, higher than predicted by a linear combination of single peak etch rates at the two energies. We attribute this to the effect of high energy ion bombardment on the chemical composition at the substrate surface, altering the competition between etching and deposition. When net deposition is suppressed, 100 eV ions will interact with the underlying substrate to more effectively enhance etching. The etch rate data provide evidence that for the process examined, a high energy group of ions, comprising as little as 25% of the total flux. produces this suppression, enabling lower energy ions to contribute to etching reactions. These results highlight the significance of the shape of the IED on plasma process outcomes.

8:40am **PS1-WeM3 Diamonds and New Carbon Allotropes from Carbon Nanotubes at Room Temperature**, ***M.J. Behr*****,* University of Minnesota, *A.R. Muniz, T. Singh, D. Maroudas,* University of Massachusetts, Amherst, *E.S. Aydil*, University of Minnesota

Interactions of reactive plasmas with nanostructured materials enable the synthesis of materials that would not be expected to form at low temperature and in vacuum. As a remarkable example, in this presentation, we report the plasma synthesis of diamonds and other new carbon allotropes from multiwalled carbon nanotubes (MWCNTs) at room temperature. We exposed MWCNTs to hydrogen atoms created by plasma dissociation of dihydrogen gas in a downstream inductively coupled plasma and observed the transformation of the nanotubes to various crystalline carbon structures, even at room temperature. Examination of the H-exposed MWCNTs with transmission electron microscopy (TEM) revealed webs of long strings of crystallites, ~2-20 nm in diameter, in locations occupied initially by nanotubes. High-resolution TEM, selected-area electron diffraction, and convergent-beam electron diffraction techniques were used to identify the lattice structures of these carbon nanocrystals as cubic diamond, cubic n-diamond, lonsdaleite (hexagonal diamond), and a new carbon allotrope with face-centered cubic symmetry and lattice parameter a = 0.426 nm. This H-induced transformation was observed over the temperature range from 300 K to 1073 K, and investigated as a function of atomic hydrogen dose. Combining synergistically our experimental findings with molecular-dynamics simulations and first-principles density functional theory calculations, we show how H atoms produced in the dihydrogen plasma can induce sp2-to-sp3 C-C bonding transitions in MWCNTs and help nucleate various crystalline carbon allotropes such as cubic diamond and lonsdaleite.

9:00am **PS1-WeM4 Clarification of Surface and Interface Structures Exposed to Inductively Coupled Plasma with Various Superposed Bias Frequencies and Its Implication in Plasma Damage Control**, ***Y. Nakakubo****, A. Matsuda, Y. Ueda, H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Plasma-induced Si substrate damage has become one of the critical issues in advanced MOSFETs with shallower junction in source/drain extension regions, since the damaged layer thickness will be in conflict with the device design margin (e.g. ~ 5 nm in 32-nm-node). The thickness is considered to be governed by plasma parameters such as ion energy distribution function (IEDF). With regard to plasma design, a plasma source driven by superimposed dual bias frequency was reported to control IEDF. For understanding the mechanism and suppressing the damage, the plasma-induced defects should be quantitatively estimated, and then, plasma should be optimized. We have preliminary quantified the damage induced by an inductively coupled plasma (ICP) reactor with superposed bias configuration by a photoreflectance spectroscopy (PRS)–based method.[1] Silicon wafers were exposed to an ICP reactor which apply bias powers with various superposed bias configurations with frequencies of 13.56 MHz and 400 kHz. The defect site density was determined by the PRS-based method. The surface and interface layers were assigned by spectroscopic ellipsometry (SE) and TEM. The surface layer growth and interfacial layer (IL) structure were studied by molecular dynamics (MD) simulation developed for the present process condition. The above structures were analyzed by stretching of capacitance-voltage (C-V) curves for the damaged samples. Based on the above comprehensive analyses, we found that an accurate model for plasma-damaged silicon surface structures should include an interface layer between the surface layer and the substrate, i.e., a conventional methodology can lead to an erroneous conclusion in addressing the structures. This bi-layer structure (surface stoichiometric SiO_2 and IL) was clarified by TEM, MD simulation and C-V test. The IL thickness increases with self-dc bias voltages. We also observed surface sputtering process (the decrease in surface layer thickness) and more severe damage at higher dc-bias voltages (> 150 V), resulting in larger defect density (~ $10^{13}cm^{-2}$) in IL. Furthermore, it was quantitatively confirmed from PRS, SE and C-V techniques that interfacial layer growth and defect generation process depend on the superposed bias configurations with the same power. Quantitative measures and consideration of IL are key to future plasma and device designs.

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@super 1@Y. Nakakubo et al., Proc. Symp. Dry Process (2007) 287.

* PSTD Coburn-Winters Student Award Finalist

9:20am **PS1-WeM5 Studying Surface Damage during Dry Etching of Si(100) with Optical Second-Harmonic Generation in an Ar^+/XeF_2 Beam Setup**, ***P.M. Gevers**, J.J.H. Gielis, H.C.W. Beijerinck, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Increasing demands due to miniaturization in the semiconductor industry continuously lead to new challenges for plasma-based dry etching. Fundamental studies help to address these challenges, e.g., by clarifying the etching dynamics on the microscopic level. Circumventing the complexity of etching plasmas by using a multiple-beam experiment, we have investigated etching of the archetypical model system of Si(100) with Ar^+ ions and F radicals using XeF_2. The surface and interface-sensitive nonlinear optical technique of second-harmonic generation (SHG) was applied to gain insight into surface related processes such as the creation of a damaged layer as well as surface defect states involving strained Si-Si bonds and Si dangling bonds. The fundamental radiation for the SHG experiments was created by an optical parametric amplifier (80 MHz, 90 fs, 0.8-1.1 eV) pumped by the regenerative amplified radiation of a Ti:sapphire oscillator. Clean H terminated Si(100) samples were exposed to well characterized beams of low energy Ar^+ ions (70-1000 eV) and/or XeF_2 radicals. During exposure to Ar^+ ions the near surface region of the c-Si was essentially converted to an amorphous layer creating a two-layer structure. The studies were performed both spectroscopically during steady state conditions and in real time under transient conditions. Previous experiments,[1,2] in the 1.3-1.8 eV energy range yielded two spatially separated contributions with a 2ω resonance around 3.4 eV associated with modified Si-Si bonds, one at the a-Si surface and one at the a-Si/c-Si interface. The present interpretation for the 0.8-1.1 eV range indicates that the main part of the SHG signal arises from the tail of those resonances, which are assigned to E'_0/E_1-like transitions. A simple exponential model for the real-time data shows that a third contribution is necessary to describe the data well. This third contribution appears to be temporary, i.e., it is only present during the build-up of the a-Si layer. It will be discussed that this temporary contribution might be associated to the creation of dangling bonds and it will be addressed how it yields insight into the development of the a-Si layer over time.

[1] J.J.H. Gielis et al., Phys. Stat. Sol. (C) 2, 3968 (2005)
[2] J.J.H. Gielis et al., Phys. Rev. B 74, 165311 (2006).

9:40am **PS1-WeM6 Ion Induced Etching Reaction of SiO_2 and Si by CF_3^+ Irradiation**, ***K. Karahashi**, S. Hamaguchi*, Osaka University, Japan

Fluorocarbon plasmas have been widely used to etch a silicon dioxide in the fabrication of semiconductor devices. In the view of the development of integrated semiconductor devices, more precise control of the etching process is required for further progress. In the previous work, the etching yield of SiO2 by CFx+ irradiation.[1] In the present work, we report measurement results of the desorbed products of SiO2 and Si etching due to the irradiation of CF3+ ions, which are considered to be the main ion species in fluorocarbon plasmas. Time of flight(TOF) measurements are also reported, which determines kinetic energies of the products. The low-energy mass-analyzed ion beam apparatus consists of an ion beam source, an ultra high vacuum scattering chamber. Various ions were generated in arc plasma of CF4 and were extracted from the ion source. CF3+ ions for sample irradiation were selected with a mass-analyzing magnet, passed through conventional beam optics, and decelerated to specified irradiation energy just before they reached the sample. Angular distribution of desorption products were detected through an aperture by a rotatable quadrupole mass spectrometer. To measure time of flight distributions of desorbed products, the ion beam is electronically chopped at deflectors in beam line When a CF3+ ion at 500 eV impinged on a SiO2 surface, the major desorbed product was SiF2. Angular distribution of SiF2 follows a cosine law, and the flux of SiF2 does not depend on the ion incident angle. On the other hands, When a CF3+ ion impinged on a Si surface with a large incident angle, the major desorbed product was Si and SiF. Angular distribution of desorbed Si and SiF strongly depends on the ion incident angle and energy. These results clearly show that the desorption process of etching on SiO2 differs from that on Si surface; collision cascades by incident ions on a surface hardly affect desorption of SiF2 from SiO2, unlike the desorption of Si atoms. This explanation of the desorption mechanism is also supported by the observation of TOF distribution measurements of desorbed SiF and SiF2. The TOF spectra of SiF and SiF2 are fitted well by collision cascade and Maxwell-Boltzmann distributions. These results indicate that the main desorption paths of SiF and SiF2 are different; SiF desorbs with collision cascade and SiF2 desorbs with thermal activation after collision cascade.

[1] K.Karahashi et al. J.Vac.Sci.Technol. A, 2004, A22, 1166.

10:40am **PS1-WeM9 Enhanced Ground and Metastable Atom Densities in Ar Diluted N_2 ICP for Nitridation of Hf Silicate**, ***T. Kitajima**, T. Nakano,* National Defense Academy of Japan, *T. Makabe*, Keio University, Japan

The nitridation of high-k HfSiO film surface by nitrogen plasma is an important process for enabling amorphous homogeneous film without phase separation at high temperatures.[1] The relation of plasma generated species fluxes toward the film surface and the nitrogen incorporation degree of HfSiON is not well characterized. The authors have previously shown that the improved film quality of plasma grown SiO_2 due to rare-gas dilution of O_2 plasmas and its relation with the increased metastable $O(^1D)$ atom flux.[2] Here we diagnose the ground and metastable N atom densities in rare-gas diluted N_2 plasmas and relate the flux components with the N incorporation to the Hf Silicates. The ground $N(^4S)$ and metastable $N(^2D)$ density in the Ar diluted N_2 ICP (70 MHz) is measured by the VUV absorption spectroscopy using 120 nm and 149.3 nm emissions from the discharge light source ($N(^4P) \rightarrow N(^4S)$, $N(^2P) \rightarrow N(^2D)$). For the gas pressure of 100 mTorr and the ICP power of 100 W, $N(^2D)$ density is 2×10^{10} cm^{-3} in pure N_2 and decreases to 1×10^{10} cm^{-3} at $N_2/(N_2+Ar)$ ratio of 0.5 while $N(^4S)$ density stays at $7\text{-}8 \times 10^{10}$ cm^{-3}. $N(^2D)$ density increases to 3.5×10^{10} cm^{-3} of maximum with the decrease of $N_2/(N_2+Ar)$ ratio to 0.1. The trend is also found for the case of He diluted N_2 plasma. The decrease of $N(^2D)$ for N_2 fraction of 100 to 50 % is due to the reduced dissociative excitation of N_2 while the EEDF is kept stable. The increase of $N(^2D)$ for N_2 fraction of 10 % is caused by the increase of high energy electrons due to the reduced energy loss by vibrational excitation of N_2. Since the $N(^2D)$ / $N(^4S)$ ratio reaches 0.5, we expect collisional excitation of $N(^4S)$ is important source for $N(^2D)$. The nitrided HfSiO films are examined by XPS and the N incorporation is correlated to the expected N atom flux to the surface. Detailed growth results are shown in the presentation.

Authors thank the Suzuki Foundation for the partial support of conducting this study.

[1] M.A.Quevedo-Lopez, J.J.Chambers, M.R.Visokay, A.Shanware, and L.Colombo, Appl.Phys.Lett., 87, 012902 (2005).
[2] T.Kitajima, T.Nakano, and T.Makabe, JVST A. (to be published).

11:00am **PS1-WeM10 Dependence of Carbon Removal Rate on the Structure of Porous Low-k SiOCH Films during N_2/H_2 Plasma Processes**, ***K. Kurihara***, Toshiba Corp., Japan

To realize highly reliable interconnects for sub 32 nm node LSI, low-k materials such as porous SiOCH films are demanded to be resistant to plasma processes, such as etching and ashing. This is because a methyl group which makes hydrophobic film is easily abstracted from the film during the plasma irradiation processes. We have examined the plasma resistance of SiOCH films which contained the methylene-bridge ($Si\text{-}CH_2\text{-}Si$) structure[1] using a plasma beam irradiation apparatus.[2] This apparatus enabled us to carry out plasma-surface interaction experimens using identified irradiation species. We used two kinds of spin-on-glass porous SiOCH films (k=2.0). One contained only methyl groups, and the other contained both methyl groups and methylene bridges. Used gas chemistry was nitrogen and hydrogen gas mixture plasma. We assumed the damage of the pattern sidewall and irradiated only neutral species from the plasma to the SiOCH films. Major irradiated neutral species were NHx (x=1-4) in addition to parent gases. We evaluated the damage of the film by using the decrease ratio of the carbon content measured as an index by XPS and FTIR. It was found that the decrease ratio of carbon in the SiOCH film contained only methyl groups was larger than that in the film contained methylene bridges. The authors thank JSR Corporation for supplying the SiOCH films.

[1] H. Miyajima et al. Proc. of Advanced Metallization Conf. 37 (2007).
[2] K.Kurihara et al. J. Vac. Sci.Technol. A 22, 2311(2004).

11:20am **PS1-WeM11 Mechanistic Influence of Substrate Temperature on the Plasma Deposition of Carbon Nitride Materials**, ***J.M. Stillahn**, E.R. Fisher*, Colorado State University

In an effort to elucidate important processes involved in plasma-enhanced chemical vapor deposition (PECVD), our lab has employed several diagnostic tools to characterize the gas phase, film properties, and gas-surface interface under similar PECVD conditions. This work focuses on the application of these tools to the particular case of amorphous hydrogenated carbon nitride ($a\text{-}CN_x$:H) materials, which have a number of potential commercial applications. PECVD of $a\text{-}CN_x$:H has been performed in inductively coupled rf plasmas using precursors that favor the formation of the CN radical, a likely contributor in the deposition process. CN was characterized in the gas phase using laser-induced fluorescence and mass spectrometry. Results suggest probable formation mechanisms and provide information about the energetics of the formed radicals. The imaging of radicals interacting with surfaces (IRIS) technique was used in these studies as a means of probing the behavior of CN radicals at the surface of the growing film under both ambient and heated-substrate conditions. These results, along with deposition rate and film composition data obtained as a

function of substrate temperature, provide a more complete understanding of the interaction of plasma species with heated substrates in these systems.

11:40am **PS1-WeM12 Examining Plasma-Surface Interactions During Plasma Catalytic Removal of Atmospheric Pollutants**, ***M.M. Morgan***, *E.R. Fisher*, Colorado State University

Nitric oxide (NO) and sulfur dioxide (SO_2) are atmospheric pollutants that are produced from engine exhaust. Improvement in catalytic treatment of exhaust gases is therefore necessary to reduce these emissions. We are using plasma-catalytic processes to aid in the removal of pollutants from exhaust gases. An understanding of the fundamental chemical gas-phase and gas-surface processes is required to address this issue. With our imaging of radicals interacting with surfaces (IRIS) technique, we can simultaneously examine the gas-phase, perform surface analyses, and probe the gas-surface interface. IRIS combines laser-induced fluorescence and molecular beam techniques, thus we can probe a variety of important atmospheric species such as NO, SO_2, OH, CH, and CN. We have used IRIS to address the fundamental issue of NO and SO_2 removal by measuring relative gas-phase densities and by examining the steady-state surface reactivity of plasma-generated species on catalytic surfaces. For example, gas phase densities for NO demonstrate a significant decrease in NO at higher applied rf powers and when additives such as H_2O and CH_4 are added to the system. Water has also been added to the gas mixtures containing NO and SO_2 to monitor the effect of OH production in these processes. Comparison of surface interaction data shows that NO scatters substantially whereas OH has a higher surface reaction probability. Substrates used include silicon wafers and a variety of catalytic surfaces such as Pt and Au. Additional optical emission spectroscopy and mass spectrometry data will also be presented on all of these systems. Preliminary IRIS data on CH and CN will also be included for comparison to NO, OH, and SO_2.

Plasma Science and Technology
Room: 306 - Session PS2-WeM

Plasma Sources
Moderator: E.A. Hudson, Lam Research, C.A. Wolden, Colorado School of Mines

8:00am **PS2-WeM1 Generating Short Wavelength Light from Compact Sources - Challenges and Applications**, ***W. Holber***, *S. Horne, M. Partlow, J. Silterra, D. Smith, J. Ye, H. Zhu*, Energetiq Technology, Inc. **INVITED**

Across a range of scientific and technological applications, there is a need for more capable short-wavelength light sources. In semiconductor manufacturing, critical dimensions are now in the nanometer range and EUV at 13.5 nm is under active investigation as a lithography source. In biotechnology, structural information on proteins requires UV down to 170 nm and internal cellular features are imaged using 2.3-4.3 nm radiation. Lasers can produce significant amounts of light at specific wavelengths in the UV, but do not provide broad wavelength coverage either in the UV or soft x-ray spectral regions. Synchrotrons are a source of bright, incoherent radiation at wavelengths from hard x-ray through DUV, but are based in large, centralized facilities. Incoherent light sources that are lab-based provide an alternative to synchrotrons in a growing number of applications. We will present results from a compact z-pinch plasma source customizable to different wavelengths in the EUV and SXR[1] range, generating up to 10 Watts of power at 13.5 nm, and a laser-driven lamp source of light from 170 to 800 nm. Both provide uniquely bright output over a range of applications.

[1] Work on SXR sources funded in part by NIH Grants 5R44RR022488-03 and 5R44RR023753-03.

8:40am **PS2-WeM3 3-Dimensional Model for Magnetized Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *J.A. Kenney, K. Collins*, Applied Materials, Inc.

Static magnetic fields are often used in plasma processing systems to improve plasma confinement, modify plasma spatial profile or adjust other plasma characteristics. Aside from some simple magnetic field configurations, magnetized plasmas have a complex spatial structure and significant physics is missed in reduced (0, 1 or 2) dimensional models. A 3-dimensional fluid plasma model is used to understand the operation of magnetized capacitively coupled plasmas operating at 13.56 and 180 MHz in this paper. Both electropositive (Ar) and electronegative (O_2) gases are considered. To simplify interpretation of results, simulations have been done for an axi-symmetric reactor geometry. Static magnetic field is generated using current carrying wires, where several wire configurations that generate converging, diverging and uniform magnetic fields in the plasma region are considered. Our 3-dimensional plasma model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential, A, are solved in the frequency domain after each cycle for multiple harmonics of the driving frequency. The coupled set of equations governing the scalar potential, φ, and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron energy equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. The effect of static magnetic field is included through the charged species transport properties, which become tensor quantities in the presence of a static magnetic field. Without magnetic field, electron density peaks in the center of the chamber when the plasma is generated using a 180 MHz source. The 180 MHz plasma is also symmetric because of considerable distance from the chamber walls. When a static magnetic field parallel to the electrodes is applied, ExB drift in the sheath regions shifts the peak in plasma density off-axis. As the 180 MHz plasma is symmetric, ExB drift occurs in opposite direction in the two sheaths, which leads to an overall shearing of the plasma. Electron density peaks near the electrode edges in the 13.56 MHz plasma and the plasma is highly asymmetric. Application of magnetic field and the resultant ExB drift lead to overall shifting of the low frequency plasma in the ExB direction.

9:00am **PS2-WeM4 Effects of Very High Frequency Source Mixing and Inter-electrode Gap on Plasma Characteristics**, ***K. Bera***, *S. Rauf, K. Ramaswamy, K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma (CCP) discharges are widely used for dielectric etching in the semiconductor industry. Very high frequency (VHF) power sources are being employed to generate plasmas for dielectric etching due to VHF's various benefits including low plasma potential, high electron density, and controllable dissociation. Electromagnetic effects tend to make the spatial and temporal behavior of VHF plasmas complex with a rich set of new physics. If plasmas are generated using multiple VHF sources, one can expect interaction between the sources and plasma characteristics to be different from those due to individual frequencies. We investigate the effects of VHF frequency mixing on plasma characteristics in this presentation. The study is done for a range of inter-electrode gaps. Both computational modeling and experiments are utilized. Our plasma model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential are solved in the frequency domain after every cycle for multiple harmonics of the driving frequency. Current sources for the vector potential equations are computed using the plasma characteristics from the previous cycle. The coupled set of equations governing the scalar potential and drift-diffusion equations for all charged species are solved implicitly in time. Plasma simulation results show that electron density is usually higher in the center of the chamber at high frequencies due to a standing electromagnetic wave. Electrostatic effects at the electrode edges tend to get stronger at low VHF frequencies. Electron energy distribution function (EEDF) appears to be two-temperature Maxwellian. Ion saturation current measurements using a Langmuir probe show that ion saturation current, and hence plasma density, peaks in the chamber center at high VHF frequencies. As power at low VHF frequencies is added, ion saturation current increases at the edge of the electrodes and electrostatic effects become stronger. Even at high VHF frequencies, inductive heating at the electrode edges becomes strong for small inter-electrode gaps. This tends to increase electron density at electrode edge relative to the chamber center. As the gap is increased, the plasma is able to diffuse to the chamber center. The electromagnetic effects that dominate near the chamber center become more important than electrostatic effects.

9:20am **PS2-WeM5 The Impact of Electrode Gap and Gas Injection on Plasma Etch Uniformity**, *G.M. Amico*, ***M. Block***, *S. Sirard, J. Guha, A. Leming, A. Marakhtanov, E.A. Hudson, M. Srinivasan*, Lam Research

At the 32nm node and below, etch rate and CD uniformity requirements for multi-layer low k dual damascene integration schemes continue to tighten. Additionally, more focus is being placed on the process uniformity at the outer 5mm of the wafer. This paper examines the effect of electrode gap and the distribution of gas injection in a capacitively coupled reactor with confined plasma and adjustable gap. Radial etch rate and CD uniformity were studied for different films, with emphasis on multi-layer DD integration schemes. Mechanisms for the influence of electrode gap on process uniformity are different for ion limited and neutral limited etch regimes. Oxide etch rate radial uniformity as a function of gap shows a correlation to ion flux measurements. Narrower gaps tend to increase edge etch rates for all films, but the gap for optimal uniformity is dependent upon film composition. For multi-layer processing, the overall uniformity can be improved by employing different gap settings for each process step.

9:40am **PS2-WeM6 2 m Long-Line Plasma Production by Evanescent Microwave in a Narrowed Rectangular Waveguide**, *H. Shindo, **Y. Kimura***, Tokai University, Japan

Long line-shaped plasmas are inevitable in material processing in manufacturing industries, such as flat panel displays (FPDs) and surface modification of large- area thin films. In this work, we studied a newly proposed method of large-scaled line plasma generation. In this method, microwave power of frequency of 2.45 GHz in a narrowed and flattened rectangular waveguide is employed to produce plasma. Since the width of waveguide is very close to the cutoff condition, the wavelength of microwave inside the guide is very much lengthened, providing a condition of long uniform line plasma generation. The narrowed rectangular waveguides of 1.5 and 2.0 m in length and 5mm in height were examined. The width of the waveguide could be varied from 59 to 61 mm. The waveguide has a long slot of 5 mm width on the top surface to launch the microwave into the discharge plasma chamber. The plasmas of Ar nad He at the pressures of 0.1 to 5Torr were generated by employing an extremely long microwave wavelength. It was observed that the microwave electric field became more uniform as the wave guide width was narrowed, indicating that the plasma production is due to the mechanism expected. The optical emission line measurements in Ar and He plasmas also confirmed that the uniform plasma was produced in the entire region of 1.5 m and 2.0 m. The probe measuremnts of the plasma were also made, indicating that the plasma uniformity was within 10 % in the entire plasma. Thus we conclude that the present method of plasma production is quite advantageous for large area processing. Plasma extraction was also successfully tested.

10:40am **PS2-WeM9 Development and Characterization of a Radical Beam Source Based on Surface Waves for Plasma-Surface Reaction Studies**, ***R. Khare***, University of Houston, *L. Stafford*, Université de Montréal, Canada, *J. Guha, V.M. Donnelly*, University of Houston

Previously, we studied recombination of Cl and O on plasma-conditioned anodized aluminum and stainless steel surfaces. Cl and O atoms formed in chlorine or oxygen plasmas impinged on a cylindrical substrate that was rapidly rotated such that points on the surface were exposed to the plasma and then to a differentially-pumped analysis chamber equipped with either an Auger electron spectrometer or a mass spectrometer. Langmuir Hinshelwood (LH) recombination was observed by monitoring desorption of Cl_2 and O_2 with the mass spectrometer or through a pressure rise. In these previous experiments, however, Eley Rideal (ER) recombination (if it occurs) could not be detected because it would take place instantaneously in the presence of atom flux, and hence would cease as soon as the sample left the plasma. To observe the ER component, as well as to isolate LH recombination in plasmas with multiple radical species (i.e. most plasmas), a separate radical beam source is needed in combination with the plasma and spinning substrate. With this in mind, we investigated a surface-wave chlorine plasma operating at 2.45 GHz and sustained in a 8 mm O.D. quartz tube using a gap-type surfatron wave launcher. With added traces of rare gases, optical emission spectroscopy was used to measure Cl and Cl_2 densities and the electron temperature, T_e, at 50 mTorr as a function of distance from the wave launcher. The Cl(792.4 nm)-to-Xe(828 nm) emission intensity ratio, reflecting the Cl number density, decreased with distance from the launcher, while the Cl_2 (306 nm)-to-Xe emission ratio that is proportional to Cl_2 number density, peaked near the launcher. The Cl_2 percent dissociation obtained from the calibrated Cl_2 -to-Xe emission ratio was very high (97 %) near the launcher, and remained high (89 %) until the end of the plasma column (about 12 cm from the launcher for an absorbed power of 90 W). By selecting Ne, Ar, Kr, and Xe lines excited from the ground state which are characteristic of the high energy portion of the electron energy distribution function (particularly Ne), we found that T_e increased from 5 to 10 eV as the observation point was moved away from the launcher. On the other hand, a nearly constant value of $T_e = 3.1 \pm 0.6$ eV was obtained using Ar, Kr and Xe lines excited to a significant extent through impact with lower energy electrons. Mechanisms for such high energy tails will be discussed.

11:00am **PS2-WeM10 Production-Worthy Pulsed ICP Plasma Processes**, ***S. Banna***, *V. Todorow, K. Ramaswamy, A. Agarwal, S. Rauf, K. Collins*, Applied Materials, Inc.

The transition to 45nm and smaller technologies has triggered intensive research effort among academic and industrial communities in search of wider range of plasma operating conditions aiming to improve etch processes for finer features. Pulsed radio frequency (PRF) plasmas are promising to achieve such a goal. It has been demonstrated through numerical modeling and basic experimental studies that PRF plasma might exhibit higher selectivity, improved uniformity, and minimal charge damage in many etch processes. However, due to the lack of efficient RF power delivery, PRF has only been utilized in a limited number of large-scale commercial applications. Particularly, two main PRF regimes were utilized in inductively coupled plasma (ICP) reactors. In the first, the source operates in the continuous wave (CW) RF mode while the bias operates in the PRF mode. In the second, the source power is pulsed while having the bias operating in the CW mode. The main challenge has been to minimize the amount of reflected power. Specifically, high bias reflected power was observed for low-pressure processes with source pulsing, in which time-modulation of the source power is highly coupled to the bias. The high reflected power is mainly due to the mechanical nature of conventional dynamic matching networks used to reduce the reflected power. The response time of the mechanical adjustment is of the order of hundreds of milliseconds. Hence, the match cannot track the changes in the time-modulated power as the pulse frequencies of interest are greater than 1kHz. There is a vital need for new capability to reduce the reflected power in sub-millisecond time scale. Recently, we have developed production-worthy, reliable and robust PRF plasma operation in a commercial ICP reactor that provides an expanded window of operation by establishing multiple techniques for optimizing RF power delivery in PRF mode. By so doing the matching response time is reduced to as low as a few microseconds. Accordingly, larger number of etch processes operating at pulsed plasma mode are feasible. The robustness of the system is manifested by its ability to provide a variety of RF modes of operation, furnishing more flexibility in etch processes design. By utilizing these modes in ICP reactor, it was demonstrated that one can improve uniformity, enhance selectivity and eliminate micro-trenching in real production etch processes. Supporting plasma modeling and diagnostics will be discussed.

11:20am **PS2-WeM11 Two Cannel Filtered Vacuum-arc Plasma Source for Composite Coatings Deposition**, *I.I. Aksenov, D.S. Aksyonov, V.V. Vasilyev, A.A. Luchaninov, E.N. Reshetnyak, **V.E. Strel´nitskij***, NSC "Kharkov Institute of Physics and Technology", Ukraine

The new two-cathode filtered vacuum arc plasma source is considered. The source contains two plasma generators with magnetic stabilization of an arc and focusing of a plasma stream. For removal of macroparticles from plasma generated the two-channel magnetic filter with T-shaped plasma duct is used. When both generators are simultaneously in operation the plasma streams emitted by them go through the entrance sections of the plasma duct into its exit section, and are transported up to a substrate. By means of a flat matrix probe the measurements of an ion current and its density distribution at the output plasma stream cross-section have been carried out. The ion current at the filter exit strongly depends on intensity and geometry of magnetic fields in the plasma guiding channels and on pressure of argon gas in the system. At arc current of 100 A of each generator the output ion current was 5.5 A. At creation of an acute-angled magnetic fields distribution with the annular cusp near the filter exit, the conditions providing leveling of the ion current density distribution at the probe surface and thickness of the condensed film distribution along the substrate surface were attained. When both generators with the cathodes of different materials (Al and Ti) were simultaneously in operation, coatings with rather homogeneous composition were grown at the motionless flat substrate of 60 mm in diameter. Aluminum percentage dispersion was about 70 %. At operation of only one generator the output plasma stream density distribution was strongly asymmetrical. The leveling and balancing of the distribution in this case also was reached by creation of the acute angle magnetic film at the system exit. At use of composite cathodes (Ti, Si) the structure of condensate deposited was non-uniform. Leveling of the components concentration distribution on a spot of condensation was reached choosing the argon pressure in the system and the substrate negative bias voltage. The gained results of researches are rather perspective for growth of high-quality composite coatings including nanostructural.

Nanomanufacturing Focus Topic
Room: 309 - Session NM+PS+AS-WeA

Nanomanufacturing I: Plasma Processing and Materials
Moderator: R.M. Martin, IBM T.J. Watson Research Center

1:40pm **NM+PS+AS-WeA1 Silicon Nanocrystal Inks: Plasma Processing as a Route to Solution-Processed Silicon Films**, ***U.R. Kortshagen***, *R. Cram, D. Rowe, X.-D. Pi*, University of Minnesota **INVITED**

Colloidal nanocrystals are studied for a wide spectrum of applications from more efficient quantum dot solar cells to printed electronics. While significant advances have been made with chalcogenide semiconductors, similar progress with silicon has been hampered for a long time by the lack of efficient synthesis approaches. However, silicon has the undoubted advantage of being non-toxic, environmentally benign, abundant and cheap. This talk describes a plasma synthesis approach for the efficient synthesis of silicon nanocrystals. Silicon crystals are synthesized in a flow through plasma reactor on time-scales of a few ms. The residence time of the silicon crystals can be used to tailor the nanocrystal size. Dopants can be introduced into the crystals and changes in the photoluminescence properties as well as surface etching studies allow to deduce the dopant location within the nanocrystal. The nanocrystal surfaces can be functionalized with organic ligands that impart solubility to the nanocrystals. By making silicon nanocrystals soluble in organic solvents, inks of doped silicon crystals can be formed that can be used to prepare silicon nanocrystal films through solution processes such as drop coating, spin coating, or ink-jet printing. Laser annealing is used to produce conducting films from the colloidal nanocrystal precursors. Structural and electrical properties of the films are determined with a wide array of characterization techniques. Properties and potential applications of these materials will be discussed.[1]

[1]This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. Partial support is acknowledged by NSF grant DMI-0556163, and by Center for Nanostructure Applications at the University of Minnesota.

2:20pm **NM+PS+AS-WeA3 Vertically Aligned Si Nanostructure Arrays formed using SF_6/O_2 Plasma**, ***C. Yang***, *S.H. Ryu, Y.D. Lim, W.J. Yoo*, Sungkyunkwan University, Korea

Arrays of high aspect ratio (>10:1) vertically aligned Si nanostructure were formed in an inductively coupled plasma (ICP) reactor using SF6/O2 plasma without any masks at noncryogenic temperature. Mean diameter of the nanostructure arrays is about 100 nm and the mean height is up to 4.77 um. These nanostructure arrays can be fabricated for large area (>100 cm2). The formation of the nanostructure arrays are studied as a function of time, bias RF-power and O2/SF6 ratio. The processing condition of the SF6/O2 plasma is known to markedly affect the preparation of the nanostructure arrays. O2/SF6 ratio determines the formation of the nanostructure arrays. The nanostructure arrays only could be fabricated when the O2 content is not too low or too high, the range is 0.5< O2/SF6<2.5. Two types of the nanostructure arrays formed because of the different bias RF-power, one is nanohole arrays and another is the nanopillar arrays. The formation of the nanostructure is hole when the bias power is 10 W, but the diameter is only 420 nm after etching 150 s. If the bias power increased to 30 W, the nanopillar arrays appear, the mean height is up to 4.77 um after etching 150s. The etching time is also important for the nanostructure arrays. After etching about 40s, the nanostructure arrays appear abruptly and become longer and longer. But very long time etching has destroyed the nanostructure arrays. The mechanism of the plasma etching for fabricating the nanostructure arrays has been investigated using OES, XPS and SEM analyses. From the analyses, the properties of the plasma and the formed passivation layer are mainly reasons for the fabrication of the nanostructure arrays. The best condition to fabricate a high aspect ratio vertically aligned Si nanostructure arrays is suggested.

2:40pm **NM+PS+AS-WeA4 Structured Growth of Silver Nanoparticles Within a Hydrocarbon Matrix**, ***E. Körner***, *J.F. Lübben, G. Fortunato, D. Hegemann*, EMPA, Switzerland

Low pressure plasma processes enable an extensive variety of surface adjustments for medical applications or technical textiles. Specifically, a modular plasma vacuum chamber provides the base for highly flexible and tailor-made coating technology. Different modification strategies, e.g. activation, etching, plasma polymerization or metallization by sputtering can be used separately or combined with each other. This work presents the combination of plasma polymerization and etching with a co-sputtering process which leads to the formation of a nanoporous polymer matrix with embedded metal nanoparticles. A capacitively coupled radiofrequency power input and an asymmetric reactor geometry allow the production of such multifunctional coatings within in a one-step process. The hydrocarbon matrix is built-up by using ethylene (C_2H_4) as a monomer gas. In addition, carbon dioxide (CO_2) or ammonia (NH_3) is used as the reactive gas, to structure the matrix and add functional groups to the a-C:H network. The deposition rate and the functionality of the coatings are adjusted by the ratio of reactive gas to monomer. With increasing the ratio of reactive gas the functionality of the matrix increases at the expense of the deposition rate. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode. The growth, distribution and formation of Ag particles are analyzed carefully under different conditions with respect to the gas mixture. The films are investigated with atomic force microscopy and scanning electron microscopy after different growth steps. It can be seen that the particles are more embedded in the matrix for higher film thicknesses and lower reactive gas ratios. Additionally, X-ray photoelectron spectroscopy analyses are performed to evaluate the surface chemistry and Ag surface concentration. For bulk measurements, the overall Ag content is measured with inductively coupled plasma optical emission spectrometry. Target covering or oxidation can decrease the Ag deposition rate and has to be taken into account in determining the optimal plasma conditions. In contrast to magnetron sputtering the Ag particles appear to be bigger with RF sputtering, which could provide a Ag reservoir with a slower release and a better long-term antibacterial effect. This is important for the application of the films as antibacterial coatings, where an optimal antibacterial efficiency for a minimal amount of Ag is desirable.

3:00pm **NM+PS+AS-WeA5 Photoluminescence Brightening from Freestanding Single-Walled Carbon Nanotube Bundles Prepared by Diffusion Plasma CVD**, ***R. Hatakeyama***, *T. Kato*, Tohoku University, Japan

The optical property of single-walled carbon nanotubes (SWNTs) has been the subject of intense interest in recent years, since the discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs. Because it was believed that the debundle of SWNTs was the inevitable process to capture the PL signal from SWNTs, the bundle forming SWNTs were, in most cases, treated as by-products or impurities causing a spectrum broadening and shifting, and hence their optical features, especially the PL, have not attracted a great deal of attentions so far. Very recently, the PL from bundled SWNTs in an aqueous solution has been reported. Since the PL from bundled SWNTs includes outstanding advantages such as an exemption from a complicated debundle process and easy manipulation, it can be expected that the SWNT-bundle engineering has a great potential for the nanotube-based PL device fabrication. From an industrial point of view, the application of nanotube-PL to the well-organized present semiconductor technology is an inevitable factor, i.e., the establishment of bright PL emission from a solid-state material is considered to be a still remainded fundamental problem. In this study we report unique PL features obtained from as-grown vertically-, and individually-freestanding SWNTs prepared by a diffusion-plasma chemical vapor deposition method.[1] The intensity of PL is clearly observed to increase through the morphology transition from isolated to thin-bundled of the freestanding SWNTs.[2] Based on the precise spectrum analysis and equation-based estimation of the PL time trace, the origin of the PL brightening is consistently explained in terms of the exciton energy transfer through the tube bundles. The PL brightening is also revealed to obviously depend on SWNT diameters. Only the small-diameter rich sample can realize the PL brightening, which can be interpreted to be due to the different concentration of metallic SWNTs causing a PL quenching. Since it appears to be possible to fabricate brightly illuminating nanotubes on various kinds of substrates, the bundle engineering with freestanding nanotubes is expected to be a potential candidate for realizing the nanotube-based PL device fabrication.

[1]T. Kato and R. Hatakeyama, Appl. Phys. Lett., 92 (2008) 031502.
[2]T. Kato and R. Hatakeyama, J. Am. Chem. Soc., accepted.

4:00pm **NM+PS+AS-WeA8 Practical Considerations for Implementation of Nanomaterials in Aerospace**, ***K.D. Humfeld***, The Boeing Company **INVITED**

4:40pm **NM+PS+AS-WeA10 Large-Scale Production and Metrology of Vertically Aligned Carbon Nanotube Films**, ***L. Dai***, *K. Bosnick*, National Research Council Canada

We have successfully produced carbon nanotube (CNT) films (25-50 wafers per load) on a large scale in a commercial Tystar chemical vapor deposition (LPCVD) system. Electron microscopy studies indicate that the CNT films

are consisted of densely packed and vertically aligned multi-walled CNTs. A series of catalysts and growth conditions are tested systematically to synthesize high quality CNTs by varying the catalytic metal compounds and the CVD parameters. Both Fe films and ternary metal Cr/Ni/Fe films have been found favorable for the growth of aligned CNT films. To assess the as-grown vertically aligned CNT films, we are developing a general metrology which contains various analytical techniques to qualify the CNT film morphology, size, chirality, homogeneity, purity, dispersion, etc. This metrology uses some of the measurement equipments that are broadly used for material characterizations, including scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, profilometry, contact angle measurement and thermo gravimetric analysis (TGA). The metrology will facilitate quality control and process optimization necessary for industry applications of CNT films.

5:00pm **NM+PS+AS-WeA11 Linewidth Measurements on sub-20 nm HSQ/Graphene Nanostructures**, ***J.J. Peterson***, Intel Corporation, *M.A. Rodriguez, V. Tileli,* University at Albany-SUNY, *M. Sprinkle, C. Berger, W.A. de Heer*, Georgia Institute of Technology

Although linewidth measurements of patterned graphene nanoribbons using the high resolution (HR) scanning electron microscope (SEM) have been reported in the literature,[1] it is known that such measurments are generally destructive to the structures which are being measured. Furthermore, due to the destructiveness of the measurement, the critical dimensions may be changing even as the measurement is being made. For this reason, the atomic force microsope (AFM) and scanning probe microscope (SPM)[2] has become an accepted method of linewidth measurement for graphene or hydrogen silsesquioxane (HSQ) on graphene structures, but this methodology is not scaleable to a manufacturing environment. For this reason, it is desired that a more manufacturable method of linewidth measurement may be developed for measurement of critical dimensions of graphene nanostructures. In this talk, we compare linewidth measurements sub-20 nm HSQ/graphene structures using the HR SEM and environmental-SEM (E-SEM) and report that E-SEM measurements will support the necessary resolution to enable linewidth measurements of graphene nanostructures without the damage associated with typical HR scanning electron microscopes. Furthermore, we make a comparison of linewidth measurements using both the SPM and E-SEM and discuss each respective method's advantages and disadvantages.

5:20pm **NM+PS+AS-WeA12 Size Distributions and Agglomeration Effects in FePtAu Nanoparticles**, ***V.V. Krishnamurthy***, Oak Ridge National Laboratory, *Z. Jia, D. Reed, M. Mandal, G.J. Mankey, J.W. Harrell, D.E. Nikles,* The University of Alabama, *L. Porcar*, NIST Center for Neutron Research

We have investigated the effect of thermal treatment on the microstructure and positional ordering of chemically synthesized $(Fe_{49}Pt_{51})_{88}Au_{12}$ nanoparticles using small angle neutron scattering (SANS). The as made FePtAu particles have an average diameter of 3 nm. Thin films of nanoparticles were prepared by spincoating the dispersion of FePtAu nanoparticle on Si wafers. The samples were annealed for 30 minutes in a flowing nitrogen atmosphere in order to promote FCC-$L1_0$ phase transformation. The annealing temperature of the samples was varied from 300 °C to 550 °C in steps of 50 °C. The crystal structure and the lattice constant of the samples have been determined by x-ray diffraction. The magnetization hysteresis has been measured in a vibrating sample magnetometer. SANS measurements were performed at room temperature with an incident neutron wavelength of 6 Å using the 30 m NG3 SANS instrument at NIST. The scattering vector magnitude (q) dependence of the SANS intensity, I(q) shows strong dependence on the sample annealing temperature. The q dependence of the SANS intensity in the range of 0.2 to 3 nm^{-1} could be fitted by modeling the nanoparticles as polydisperse spheres with Schultz distribution for the diameters and a hard sphere interaction between the particles. In this q range, the agglomerates are assumed to be polydisperse spheres. The results indicate that significant agglomeration occurs in all the samples. The average size of the agglomerates is found to increase from 18 nm at 300 °C to 53 nm at 550 °C. The data also seem to indicate the sintering of particles in the temperature range of 500-550 °C. These results will be compared with the particle size distributions in off-situ annealed $Fe_{49}Pt_{51}$ nanoparticles and in-situ annealed $(Fe_{49}Pt_{51})_{88}Au_{12}$ nanoparticles.

Plasma Science and Technology
Room: 304 - Session PS1-WeA

Fundamentals of Plasma-Surface Interactions II
Moderator: S.M. Han, University of New Mexico

1:40pm **PS1-WeA1 Adsorption and Desorption Dynamics of Atomic and Molecular Chlorine on Plasma-Conditioned Stainless Steel Surfaces**, ***L. Stafford***, Université de Montréal, Canada, *R. Khare, J. Guha, V.M. Donnelly,* University of Houston, *J.S. Poirier, J. Margot*, Université de Montréal, Canada

We investigated the interactions of atomic and molecular chlorine with plasma-conditioned stainless steel surfaces through both experiments and modeling. The adsorption and desorption dynamics of Cl and Cl_2 was characterized using a rotating substrate technique in which portion of the substrate surface is periodically exposed to an inductively coupled chlorine plasma and to an Auger electron spectrometer in separate, differentially-pumped chambers. After several hours of exposure to the Cl_2 plasma, the stainless steel substrate became coated with a Si-oxychloride-based layer (Fe:Si:O:Cl = 1:7:15:6) due to chlorine adsorption and the slow erosion of the silica discharge tube. Analysis of products desorbing from this surface through measurements of pressure rises in the Auger chamber as a function of substrate rotation frequency showed significant adsorption and desorption of Cl_2 with the plasma off, with sticking coefficients comparable to those obtained previously on plasma-conditioned anodized aluminum. Desorption rates were however much higher on stainless steel, probably because of its smoother surface morphology. When the plasma was turn on, a much larger pressure rise was observed due to delayed (i.e., Langmuir-Hinshelwood) recombination of Cl atoms. Recombination coefficients, γ_{Cl}, ranged from 0.004 to 0.03 and increased with Cl-to-Cl_2 number density ratio before reaching some plateau for $Cl/Cl_2 > 0.6$. A similar behavior was previously observed on plasma-conditioned anodized aluminum. This set of gamma values was then applied to the modeling of high-density chlorine plasmas with large stainless steel or anodized aluminum surfaces exposed to the plasma. The model is based on fluid equations in which the particle balance equations for electrons, Cl, Cl_2, Cl^+, Cl_2^+, and Cl^- are solved together with the corresponding flux equations and the energy balance equations. Using the gamma values determined in this study as a function of Cl/Cl_2 number density ratio, model predictions of Cl and Cl_2 densities in surface-wave and inductively coupled plasma reactors with both stainless steel and anodized aluminum walls will be compared with measured Cl and Cl_2 densities.

2:00pm **PS1-WeA2 Effect of Cu Contamination on Recombination of O Atoms on Plasma Conditioned Surfaces**, ***J. Guha***, *R. Khare, V.M. Donnelly,* University of Houston, *L. Stafford,* Universite de Montreal, Canada, *S. Sirard, D. Wei, G. Delgadino, E.A. Hudson*, Lam Research Corporation

Advanced dual-damascene integration schemes require patterns to be transferred through organic masks and anti-reflection coatings as well as through inorganic dielectric materials. During plasma etching of dielectrics down to underlying Cu layers, sputtered Cu may coat the reactor walls, causing process drift. In a CCP etch reactor, it was found that the photoresist (PR) etch rate drops for an O_2-based plasma process, after the plasma reactor has been exposed to Cu-containing wafers. Also the local PR etch rate is depressed opposite a Cu coupon attached to the upper electrode. The decrease in etching rate suggests that Cu could cause a decrease in the etchant concentration in the plasma, perhaps due to an increase in the heterogeneous atom recombination rate on the chamber walls. We have therefore studied the effects of traces of Cu on O recombination on an oxygen plasma-conditioned surface, using the spinning wall technique. With this method, a cylindrical spinning substrate (in this study, stainless steel coated with oxygen, as well as silicon from etching of the discharge tube) is rotated through differentially pumped chambers, allowing the surface to be periodically exposed to a 5mTorr, 600W O_2 plasma, an Auger spectrometer, and a Cu PVD source. With no Cu on the surface, a pressure rise was observed in the Auger chamber, due to desorption of recombined O_2. This pressure rise was converted into an absolute desorption flux through calibrations and was measured as a function of substrate rotation frequency. With separate measurements of absolute O-atom impingement fluxes, a Langmuir-Hinshelwood recombination coefficient of $\gamma_O = 0.10$ was derived for the steady-state, Cu-free surface, coated with a layer with an atomic composition of Fe:[Al+Si]:O ~ 1:2:9. This surface was then exposed to a Cu dose of $\sim 10^{11}$ cm^{-2}, depositing a small fraction of a monolayer (~5 x $10^{14}cm^{-2}$), which is well below the detection limit by Auger analysis (~0.1 monolayers). This trace amount of Cu caused a 13% increase in γ_O The surface was further exposed to the Cu doses of ~2, 3, and 8 x 10^{11} cm^{-2}. Each added dose causes γ_O to increase accordingly. At 8 x

10^{11}cm^{-2} γ_O = 0.15. Much larger doses (~3 x 10^{13} cm^{-2}) resulted in detectable Cu on the surface and a γ_O of ~0.3.

2:20pm **PS1-WeA3 Impact on Wafer to Wafer Repetability of Cleanning/Coating Strategies in a 300mm ICP Plasma Reactor**, ***L. Babaud***, ST Microelectronics/CNRS-LTM France, ***P. Gouraud***, ST Microelectronics France, ***O. Joubert, E. Pargon***, CNRS-LTM France

Nowadays in microelectronics, work focuses on the optimization of the 32 nm technological nodes and below. One of the key challenges to achieve the desired performance is to optimize well controlled and repeatable plasma etching processes leading to critical dimension control in the nm range. In gate etching processes one of the key parameter directly driving the process repeatability is the chamber reactor conditioning. Indeed, previous studies have shown that changes in the chamber wall conditioning are identified as one of the main origin of process drift leading to variations of key process parameters (etch rate, etch profiles, selectivity, and uniformity) inducing wafer to wafer variability. In this presentation we propose to investigate different chamber wall coating strategies such as SiOCl or Carbon rich coated films in 300 mm industrial ICP reactors. Correlation between morphological results and passivation layer formation on the silicon gate etch sidewalls using both type of coatings are performed using 300 mm in-situ XPS dedicated to chemical topography analyses. In addition, we will investigate the impact of the plasma chemistry on the process repeatability by investigating more specifically the influences of the SiCl4/O2 ratio used for chamber wall coating and of the SF6/CHF3 ratio used during poly gate patterning.

2:40pm **PS1-WeA4 Synergistic Mechanisms of Plasma-Polymer Interactions**, ***D.B. Graves***, University of California at Berkeley **INVITED**

Plasmas have been widely used to alter polymer surfaces and films, but relatively little is known about mechanisms. The interactions of low temperature, chemically reactive plasmas with polymers are generally more complex than interactions with inorganic materials. Polymers have macromolecular structure that is generally completely altered in the near-surface region by exposure to plasmas. Ions impacting the polymer surface with tens to thousands of eV coupled with fluxes of reactive radicals, electrons and photons create a vast range of potential alterations. These effects can be localized within nanometers of the surface with initial alterations that are completed within a picosecond, or can be extended in space (depth) and time over many orders of magnitude. In this talk, I will focus on recent results from both experimental and computational studies of plasma-polymer interactions in my laboratory. Molecular dynamics simulations of argon ions impacting simple polymer structures help interpret corresponding ion beam-polymer exposure experiments. Vacuum ultraviolet radiation from plasmas has recently been shown to play a key role under some conditions in roughening PMMA-based 193 nm photoresist in the presence of ion bombardment and heating. We have also studied the effects of radicals and electrons as well as the role of polymer temperature in polymer degradation, etch and roughening mechanisms.

4:00pm **PS1-WeA8 Fluorination Mechanisms of Al_2O_3 and Y_2O_3 Surfaces by Irradiations of High Density CF_4/O_2 and SF_6/O_2 Plasmas**, ***K. Miwa***, *N. Takada, K. Sasaki*, Nagoya University, Japan

Al2O3 is a typical wall material for plasma processing chambers. Interactions between the surface and fluorine-based plasmas would result in process drifts and/or particle generations.[1,2,3] Recently, replacing Al2O3 by Y2O3 was tried in an etching tool.[3] However, the interaction mechanisms have not been examined in detail. We studied the mechanisms and compared the robustness of Al2O3 and Y2O3 against the irradiation of high density fluorine-based plasmas excited by a helicon wave.[4] In the experiment, an rf power at 13.56MHz (2kW, 10Hz pulse) was supplied to a helical antenna around a quartz tube of 1.6 cm inner diameter. A uniform magnetic field was applied, so that the plasma was confined radially. A sample piece (25 mm squared Al2O3 or Y2O3) was placed on the end plate of the experiment chamber. The total pressure of CF4 (or SF6) and O2 was 7 mTorr. The duration of the irradiation was 2 hours. The sample surfaces were analyzed by XPS. On the Al2O3 surface irradiated by the CF4/O2 plasma column, fluorinated (AlOxFy and/or AlFx) and metallic Al were detected at relative concentrations of 11 % and 1.6 %, respectively. In the outside area of the irradiation, concentrations of those were 5.7 % and 1.1 %. On the contrary, lower concentrations of those were observed by the SF6/O2 plasma. These results suggest that CFx (x=1-3) radicals react with Al-O with the ion bombardment in the plasma column. The fluorination would be induced by the reaction between carbon and oxygen. In contrast, reaction probabilities between SFx (x=1-5) radicals and Al-O would be lower than that of CFx, since the bonding energy of S-O (549 kJ/mol) is much lower than that of C-O (1077 kJ/mol). In addition, the metallic Al might be induced from the fluoride by high-flux bombardment of low-energy ions.[5] On the other hand, in both irradiations of CF4/O2 and SF6/O2 plasmas onto the Y2O3 samples, the relative concentrations of fluoride (YOxFy and/or YFx) and metallic Y were much lower than the concentrations of aluminum fluoride and metallic Al on the Al2O3 samples. The results can be attributed to the fact that Y-O bonding energy is larger than that of Al-O (512 kJ/mol). In other words, Y2O3 is more robust than Al2O3.

[1]G. Cunge, et. al., Plasma Sources Sci. Technol. 14, 599 (2005)
[2]K. Miwa and T. Mukai, J. Vac. Sci. Technol. B 20, 2120 (2002)
[3]K. Miwa, et, al., Proceedings of the IEEE. ISSM 2007, PO-O-210, 479 (2007)
[4]M. Aramaki, et. al., Jpn. J. Appl. Phys. 43, No.3, 1164 (2004)
[5]J. Roth, et. al., Nucl. Fusion, 36, No. 12, 1647 (1996)

4:20pm **PS1-WeA9 193 nm Resist Modification Induced by Ballistic Electrons in a DC+RF Hybrid Etcher**, ***M. Honda***, Tokyo Electron AT Limited, Japan, ***K. Yatsuda***, Tokyo Electron Limited, Japan, ***L. Chen***, Tokyo Electron America Inc.

193 nm photoresist (PR) has low plasma etching tolerance. Resist bending, wiggling and poor etch resistance are serious problems in semiconductor manufacturing. The DC+RF Hybrid is a capacitively coupled plasma etcher with a superimposed DC voltage. This configuration was proven to be most effective for maintaining PR integrity during etching. A high negative DC bias is applied to the upper electrode. Secondary electrons emitted from the electrode surface under intense ion bombardment, are accelerated in the sheath and consequently injected into the bulk plasma, forming a ballistic electron beam. This paper presents an investigation of the mechanisms by which a 193 nm resist is modified as a result of exposure to the ballistic electrons. Various surface analytical techniques (SEM, FTIR, Raman, and SIMS) were employed. In addition, simulations were used to calculate the energy dependence of the penetration depth of electrons, ions and UV into the PR. There was no observed modification of the PR under plasma etching without DC bias. On the other hand, the thickness of the modified PR layer increased with increasing DC voltage. The modified depth of the PR layer was in good agreement with the electron penetration depth obtained from Monte Carlo simulations. The observed PR modification was not due the energetic ions, since the modified depth was much greater than the ion penetration depth, obtained from Monte Carlo simulations. In addition, the UV intensity did not correlate with the modified layer thickness. In conclusion, ballistic electrons play an essential role in modifying 193nm resist during etching using a Hybrid DF+RF etcher. By implementing this etcher, many of the critical issues related to the 193nm resist were eliminated.

4:40pm **PS1-WeA10 Impact of UV Plasma Light on Photoresist Pattern Linewidth Roughness during Gate Etch Processes**, ***E. Pargon***, *M. Martin, K. Menguelti, X. Mellhaoui, A. Bazin, O. Joubert*, LTM/CNRS, France, ***J. Foucher***, LETI/CEA, France

Typical Polysilicon/gate oxide transistors in integrated circuits are made using a sequence of lithography and plasma etching steps. The decrease in critical dimensions (CDs) of integrated circuits imposes incredibly stringent requirements on lithography and etching processes. According to the International Technology Roadmap for Semiconductors (ITRS 2007), the gate CD for high performance logic devices will be 13 nm for the 32 nm technological node and requirements for linewidth roughness (LWR) will be of 1 nm (3σ). Best lithographic processes result in resist LWR of 4.5 nm (3σ) (measured by CD-SEM). Furthermore, it is now demonstrated that the roughness of the resist pattern sidewalls is partially transferred into the active layers of the gate stack during gate etch processes, impacting significantly the final device performance. In this study, CD-AFM is used to investigate the LWR generated during the lithography and plasma etching steps involved in the patterning of the gate transistors. CD-AFM is a technique that can measure LWR values by scanning resist patterns in 3 dimensions while CD-SEM techniques only bring information in 2 dimensions. Using appropriate experimental protocols, LWR can be estimated at +/- 7% by CD-AFM technique. Our results demonstrate that the efforts to minimize the final gate LWR can be largely concentrated on the etching steps preceding those used to pattern the active materials of the gate stack (Polysilicon, metals, High K) and more particularly those involving the photoresist patterns. Our results demonstrate that LWR of photoresist patterns can be strongly minimized during plasma exposure. For instance, after HBr or Ar plasma cure, the resist sidewalls can be smoothed leading to a decrease in LWR roughness of about 10%, while HBr/O_2 resist trimming processes will induce a 50% decrease in LWR (initial LWR ranging from 18 to11 nm) strongly minimizing the final LWR of the gate. Experiments using MgF2, Sapphire and glass windows to separate the influence of plasma radiation from the impact of ions and radicals reveal that UV light emitted by the plasma plays a crucial role in the resist pattern smoothening. Since the other materials involved in the gate stack are less sensitive to UV plasma light, our results demonstrate that the decrease in LWR can be mainly monitored by working on the plasma etch steps involving the photoresist, i.e resist trimming, BARC and hard mask opening steps.

5:00pm **PS1-WeA11 Influences of UV Photon Irradiation to ArF Resist during Plasma Etching Processes**, ***K. Koyama***, *B. Jinnnai, S. Samukawa*, Tohoku University, Japan

By the downscaling of semiconductor devices, the ArF excimer laser (193 nm) lithography is now used in the fabrication of sub-100-nm devices. For the ArF lithography, chemical amplification resist is widely used. Differing from the conventional resist, the chemical amplification resist consists of photo acid generator (PAG) which generates photo-acid by UV photon irradiation. Photo acid undergoes a large number of chemical reactions through the acid-catalyzed reaction. In other words, the chemical amplification resist is very sensitive to UV photons. However, during the plasma etching process the ArF resist has serious problems, such as the low etching selectivity for underlying materials and the enhancement of line edge roughness (LER) because it is very weak against reactive plasma irradiation. In order to overcome these issues, it is essential to understand the mechanism of surface reactions for ArF resist during plasma etching processes. In this study, we investigated the effects of UV photon irradiation on the etching selectivity of ArF resist during plasma etching processes by combination of our developed neutral beam etching and conventional plasma etching. Samples were etched by chlorine atom beam (without photon irradiation) and chlorine plasma (with photon irradiation). The etching rate in the neutral beam process was much lower than that in the plasma process, and the etching selectivity of ArF resist in the neutral beam process is drastically improved, as compared with that in the plasma process. Furthermore, to clarify the effects of UV photon irradiation on the ArF resist, we investigated the changes in the chemical bonding state in ArF resist films by using FTIR spectroscopy. In the plasma processes, C-H bonds of alicyclic group and ester C=O bonds in the ArF resist film drastically decreased compared with neutral beam process. Based on these results, we found that UV photon irradiation caused breaking C-H and C=O bonds and degraded the etching selectivity of ArF resist to the etching materials.

5:20pm **PS1-WeA12 Role of Ion Bombardment Energy in Surface Roughening during Plasma Etching of Polymers and Silicon**, ***Y.H. Ting***, *C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpsel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Surface roughness in plasma etching is a critical issue for fabrication of nanoscale features. Surface roughness can degrade the electrical and optical performance of nano-devices, and can be a benefit in other applications such as study of biomimetic cellular response to surface topography, surface-enhanced Raman spectroscopy and fabrication of super-hydrophobic surfaces. The theme of this study is the role of ion energy in roughness of polymer surfaces etched in oxygen and fluorine-based plasmas, while prior studies of roughness have included the role of ion to neutral flux ratio at the surface, passivation, pressure, gas mixture, etc. Polystyrene (PS) and polymethyl-methacrylate (PMMA) are of particular interest here for block copolymer lithography of nano-scale features using PS-b-PMMA diblock copolymers, and etching of these materials is contrasted with silicon plasma etching. An rf bias on the substrate electrode, with voltage waveform tailored to provide a narrow ion energy distribution (IED), is employed to enable precise energy selection of bombarding ions. The dependence of surface roughness on bombarding ion energy has been observed using AFM for PS and PMMA during oxygen and fluorocarbon-based plasma etching using the tailored waveform. Based on NEXAFS and XPS measurements of the chemical composition of etched surfaces, we conclude that in oxygen plasma etching, localized oxidation of the PS produces a micromask that enhances roughness, and that roughness is then amplified by shadowing of neutral etchants by the topographical features. As ion bombardment energy increases above the etch onset energy in both oxygen- and fluorocarbon-based plasmas, the thickness of the steady state passivation film, measured with XPS, has been shown to decrease, and surface roughness diminishes. At higher ion energies, the dependence of surface roughness on ion energy differs qualitatively between different materials and gas mixtures. For example, the surface roughness of PMMA increases with increasing ion energy in an oxygen plasma while silicon roughness decreases with increasing ion energy in SF_6 plasmas. Published models of etching and roughening mechanisms will be evaluated by comparison with our measurements of roughness as a function of bombarding ion energy, as well as with other published results. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

Plasma Science and Technology
Room: 306 - Session PS2-WeA

Plasma Diagnostics, Sensors, and Control I
Moderator: J.P. Booth, Lam Research Corporation

1:40pm **PS2-WeA1 Novel On-Wafer RF-Current Sensor: Sheath Impedance and Plasma Density**, ***M.J. Titus***, *D.B. Graves*, University of California, Berkeley

"On-wafer" plasma sensors are new metrology tools that provide spatially-resolved wafer-state and/or plasma information. Measuring the temporal and spatial evolution of wafer-surface and adjacent plasma characteristics is the key to developing advanced plasma tool control schemes. One such commercially available sensor is the PlasmaVolt™ device, developed by KLA-Tencor. We utilize a 150 mm diameter version of the commercial product consisting of an on-board electronics module with wireless communication that allows data storage of 2 RF-current sensors embedded on the wafer at different radial positions. We report results using this device in an inductively coupled plasma with RF-biased substrate under a range of conditions. Electron density and temperature are independently measured above the wafer using a Langmuir probe and the positive ion current to chamber walls is measured with a shielded planar probe. The RF-voltage and current waveforms applied to the substrate are measured with a digital oscilloscope. The quantitative relation between the PlasmaVolt™ sensor wafer measurement and the adjacent electron density is established using a fluid sheath model. We demonstrate with this combined experimental-modeling approach that the plasma density scales with the RF-current sensor measurements but the nature of the scaling is dependent on the sheath impedance. When the sheath impedance is predominately capacitive (corresponding to relatively low electron density and high RF-bias voltage) sensor measurements are proportional to the square-root of the electron density. When sheath impedance is more resistive (corresponding to relatively high electron density and low RF-bias voltage), the sensor measurement is proportional to electron density.

2:00pm **PS2-WeA2 In-situ Diagnostic to Measure Charging During Plasma Etching**, ***E. Ritz***, *M.J. Neumann, J.A. Hoban, D.N. Ruzic*, University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, it is known that defects can occur such as trenching, bowing, and twisting. These defects are particularly noteworthy in the manufacture of DRAM deep-trench capacitors. In order to investigate the role of charging on these phenomena an in-situ diagnostic was fabricated using photolithographic and deposition techniques. The device consists of alternating layers of conducting and insulating materials. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The insulating layers create discrete measurement layers, provided by the conducting layers (electrodes). The electrodes are attached to voltage measurement leads and can then be used to measure the build up of sidewall charging at different heights along the via when exposed to a plasma. To determine the effect of geometry, if any, on charging, several aspect ratios were used by maintaining the same device thickness but varying the diameter of the vias. The entire stack is less than one micron thick, with vias ranging in diameter from 1 micron to 100 nanometers, thereby producing aspect ratios of 1:1 to 10:1. In addition, a macroscopic parallel to the diagnostic was constructed in order to compare how overall size of the features affects the charging properties. The macroscopic device is on the order of 1cm thick with features on the order of 1mm in diameter. The transition from macroscopic to microscopic gives a better understanding of the transport and charging phenomena involved in constructing DRAM features and at what scale they are significant. Conducting layers for the macroscopic device are metal and the insulating layers are ceramic. Plasma and charging experiments were conducted in a commercial silicon dioxide etch chamber. Typical ion fluxes measured on the order of 10^{17} ions/cm^2*sec. At 500W of 2.0 and 2.2 MHz power on each of the coils (1000W total), a plasma density of $2*10^{12}$ +/- $5*10^{11}$ cm^{-3} and electron temperature of 3 +/- 0.3eV was measured at 0.3+/-0.2 mm about the substrate at 4.5+/-1 cm from the edge of a 20cm chuck. RF variations in the signal were observed at the two driving frequencies and at the beating frequency of 150kHz, as expected. Results from the diagnostics will be shown for various plasma conditions and compositions.

2:20pm **PS2-WeA3 Time Dependence of Charge-Build-up Voltages in Production Etcher by On-Wafer Real Time Monitoring System**, ***J. Hashimoto***, *T. Tatsumi, S. Kawada, N. Kuriyama,* Miyagi Oki Electric Co., Ltd., Japan*, I. Kurachi,* Oki Electric Industry Co., Ltd., Japan*, S. Samukawa*, Tohoku University, Japan

Charge-build-up during plasma etching process is one of crucial issues to realize nano-scale devices. Because gate insulator thickness of such devices is shrunk down to 1nm range, the gate insulator breakdown caused by the charge-build-up is a key issue and has to be solved. To understand the phenomenon of the charge-build-up, it is absolutely necessary to monitor the time dependence of charge-build-up precisely. We have advanced charge-build-up monitoring sensors proposed by Dr.Samukawa. We have monitored etching parameters dependency and aspect ratio dependency in steady status in production etcher and have demonstrated effectiveness of the sensors. However, it was difficult to monitor charge-build-up phenomenon in unsteady status in detail. Therefore, we developed On-Wafer Real Time Monitoring System which can measure the data of charge-build-up voltages at the timing of several micron seconds and can record charge-build-up voltages in processing in production etcher. In general, the recipes in production etchers have several sequential etching steps. Unstable plasma tends to occur especially at the time of chucking wafer electro-statically, turning on-off plasma discharge and switching the etching step. As a result, they induce plasma damages. Therefore, it is important to monitor charge-build-up voltages not only in steady status, but also in unsteady status. In this study, we monitor the time dependence of charge-build-up voltages in processing in production etcher by On-Wafer Real Time Monitoring System and the charge-build-up phenomena in unsteady status will be discussed in detail in the presentation.

2:40pm **PS2-WeA4 Origin of Electrical Endpoint Signals in Rf-biased, Inductively Coupled Plasma Etching**, ***M.A. Sobolewski***, *D.L. Lahr*, National Institute of Standards and Technology

When a plasma etch consumes one layer and exposes an underlying layer, changes are detected in measured electrical parameters, such as the dc self-bias voltage and the voltage, current, impedance, and phase at the fundamental and harmonic frequencies. Consequently, these electrical signals are widely used for endpoint detection, i.e., for determining when to terminate an etch. However, the mechanisms responsible for the observed electrical changes are not well understood. The electrical changes may indicate a change in plasma electron density and ion flux caused by changes in the gas-phase densities of etch products and reactants that occur as an etch proceeds to completion. Alternatively, changes in substrate electrical properties or surface properties such as work function and the yield of secondary and photoemitted electrons may be involved. To investigate these mechanisms, experiments were performed in an inductively coupled plasma reactor equipped with rf bias and a wave cutoff probe. The cutoff probe[1,2] allowed small changes in the plasma electron density to be measured with good accuracy and resolution, on a time scale of a few seconds, regardless of the presence or absence of insulating layers on probe surfaces. Simultaneous measurements of electrical signals and cutoff probe data were made during CF_4/Ar plasma etches of thermal silicon dioxide films on silicon substrates. Changes observed in the components of voltage, current, impedance and phase at the rf bias frequency were related to, and fully explained by, changes in plasma electron density measured by the cutoff probe. The dc self-bias voltage and harmonic signals showed more complicated behavior that cannot be explained solely by changes in plasma electron density. The results allow several general conclusions to be drawn about the relative reliability and usefulness of endpoints obtained from each of the different electrical signals.

[1] M. A. Sobolewski and J.-H. Kim, J. Appl. Phys. 102, 113302 (2007).
[2] J.-H. Kim, S.-C. Choi, Y.-H. Shin and K.-H. Chung, Rev. Sci. Instrum. 75, 2706 (2004).

3:00pm **PS2-WeA5 Local and Non-Local Changes of Plasma Parameters in an Expanding Thermal Plasma Reactor Coupled with a Pulse-Shape Substrate Biasing Technique**, ***P. Kudlacek***, *R.F. Rumphorst, M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

The control of the flux and energy of ions bombarding the substrate is crucial to enhance deposited film properties or etch rate at, for example, low substrate temperatures or in weak remote plasmas. The most widespread method for these purposes is biasing because of its simplicity and suitability for operation with both conductive (dc bias) and dielectric (rf or pulsed bias) substrate. Recently, pulsed bias became subject of increased interest mainly due to lower and controllable heat load of the sample and, considering that rf bias inherently leads to bimodal energy distribution of ions bombarding the biased substrate (IED), also a promising technique to reach narrow almost unimodal IED. When pulse-shaped bias voltage is connected to the substrate holder the sheath rebuilding at the beginning of on-pulse and the ion-induced secondary electron emission during the pulse can lead to production of significant amount of fast electrons which can non-locally affect the plasma and near-wall sheath potential as has been reported by Demidov at al. (2005 Phys. Rev. Lett. 95 215002). Therefore, an effect of local and non-local changes of plasma parameters in a reactor with substrate holder biased by pulse-shaped voltage was studied in this work. Non-local changes are discussed on the basis of the electron temperature T_e and ion density n_i which are determined spatially using a double Langmuir probe technique, while the distribution function of ions bombarding the biased substrate shows local effects of biasing such as additional generation of ions driven by bias voltage and influence of collisions. IEDs are measured by means of a retarding field energy analyzer. Two limit biasing conditions are presented for comparison, namely dc bias and 13.56 MHz rf bias which shows practically no and strong (e.g. almost 5 times higher T_e in the distance of 30cm from the biased substrate holder) non-local plasma parameters affection, respectively. All experiments were run in a remote expanding thermal plasma (ETP) reactor, in Ar and Ar/N_2 gas mixture compositions under several pressures (up to 35 Pa). The substrate holder was negatively biased (up to -300V) by means of a home designed pulsed power supply operating with a frequency of up to 200 kHz and a variable duty cycle.

4:00pm **PS2-WeA8 Plasma Diagnostics by a Coaxial Resonant Cavity**, ***S. Kobayashi***, Applied Materials Inc.

Microwave plasma diagnostics were developed mainly in the field of microwave and plasma interaction. Recently, these methods have also been adopted for plasma dischargers. The main advantages of microwave diagnostics are; (a) the capability to measure directly a plasma electron density and, (b) the applicability in a process gas environment. Intended to use in dischargers, new devices (e.g. plasma absorption probe, U-shape probe, plasma microwave interferometer) were developed based on the microwave method in the last decade. However, when these open structural probes are used in a small chamber, radiation from the probe surface cannot be neglected, resulting in random resonances caused by interference with a chamber wall. To resolve this issue, a coaxial resonant cavity is developed, which is open for plasma diffusion, while it is closed with respect to microwave radiation. In vacuum, the cavity is designed to have a sharp resonance in a 2-4 GHz band. When plasma is generated in a chamber, the resonant frequency up-shifts due to a change in the effective dielectric constant. Once the resonant frequency is given as a function of a loaded electron density, the electron density is measured by monitoring a frequency-shift. Preliminary measurements of electron plasma density of Argon and Nitrogen showed good agreements with those of a Langmuir probe. Theoretically, this probe can measure the electron temperature of a plasma, since the electron temperature can be represented as a function of variation in the quality factor of a resonance in the cavity. This possibility will be also studied and discussed in the paper.

4:20pm **PS2-WeA9 On Detection and Prevention of Plasma Instabilities**, ***V.L. Brouk***, *D.C. Carter, R.L. Heckman*, Advanced Energy Industries, Inc.

The presence of instabilities in low pressure (5 to 100 mT) electronegative plasmas is well documented. In inductively driven plasmas instabilities often exist between the stable low density, capacitive mode and the stable high density, inductive regions causing oscillations in particle density, optical emission and coil voltage. Instabilities also occur in capacitively coupled plasmas driven similarly by electron attachment to electronegative species. Oscillation frequency can range from less than a 100 Hz to greater than 10 kHz and can depend on multiple process parameters including pressure, gas flow, gas mixture and power level.[1,2] Especially for high efficiency, switch mode power amplifiers, interaction between the power-dependent plasma impedance and the load-dependent amplifier response can promote or aggravate unstable behavior. This interaction involves complex impedance trajectories having both magnitude and angle components when displayed in the impedance plane. The common practice of adjusting transmission cable length shifts the phase angle of the amplifier portion of the interaction and thus minimizes the combined feedback to achieve a stable operating state. For a singular set of conditions, the point of transition from one mode to the next can be well defined and effectively addressed in this manner. But complete mapping of such behaviors across a broad process space is not practical due to the enormous number of variables present in modern plasma processes. Further, adjustments of physical cable length can be problematic in many applications. For these reasons a convenient means for predicting the onset of plasma instabilities and ideally a method for avoiding an unwanted transition to unstable operation is desirable. In this study we demonstrate a quantitative diagnostic for assessment of plasma stability providing a measure of margin from an unstable threshold. When used with a properly equipped RF amplifier, the technique provides context necessary to avoid the onset of instability in these plasmas. Using a fixed transmission cable and minor adjustments in RF frequency to adjust the electrical wavelength, we show how this method

can be used to actively stabilize both low and high frequency plasma oscillations.

[1] A. M. Marakhtanov, et. al., J. Vac. Sci. Technol. A 21 (6), Nov/Dec 2003, 1849-1864.
[2] A. Descoeudres, et. al., Plasma Sources Sci. Technol. 12 (2003), 152–157.

5:00pm **PS2-WeA11 Secondary RF Plasma Assisted Closed-Field Dual Magnetron Sputtering System for ITO Thin Film Deposition on Plastic Surfaces**, ***L. Meng********, *R. Raju,* University of Illinois at Urbana-Champaign, *T. Dockstader,* Kurt J Lesker Company, *H. Shin, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Since the demand keeps growing for larger size plasma displays, and for inexpensive flexible displays on plastic or other organic substrates, it is important to develop a plasma processing device to handle large size substrates, while maintain the uniformity and quality of deposited materials without damaging the substrate. An RF plasma-assisted closed-field dual magnetron sputtering system investigated in this study is the prototype of such a system. The prototype consists of two 3 inch DC magnetrons which can be operated at both balanced and un-balanced (closed-field) configurations. This system enhances the plasma density, metal ionization fraction and has the ability to produce high quality films at lower substrate temperature. An RF coil was fabricated, installed in between the magnetrons to initiate secondary plasma. A RF compensated Langmuir probe was used to diagnose the spatial distribution of argon sputtering plasma. In the constant current mode (50 mA) of the magnetrons, the RF plasma enhances the electron density to one-order of magnitude higher compared with no RF plasma and results in an increase in the deposition rate. The ionization fraction of the sputtered materials was measured using the QCM combined with electrostatic filters. The presence of RF plasma effectively enhanced the ionization fraction of the sputtered metal flux to about 90%. The performance of the closed-field magnetron configuration was compared with the balanced one. Enhancement in the electron density is observed in the closed-field magnetron configuration near the substrate which is twice as large compared to the balanced one. Experiments were conducted on the deposition of ITO on glass and plastic substrates at closed-field configuration. Wide range of operating parameters has been investigated to get highly transparent and conducting films. ITO thin film with 91% of transparency and resistivity of 30 Ω/square was obtained at the magnetron current of 90 mA, pressure of 5 mTorr, 2.5% of O_2 fraction in Ar, the RF power of 225 W, and substrate temperature was well kept below 120 °C. Results on the optimization of the operating parameters for high quality ITO film will be presented. Surface morphological studies have been carried out on the film using both balanced and un-balanced configurations. Results from extending this system to larger rectangular shaped magnetrons in a real flat panel display manufacturing system will also be presented.

5:20pm **PS2-WeA12 Optical and Electrical Diagnostics of an Arc Plasma Jet under Atmospheric Pressure**, ***C.Y. Wu***, National Taiwan University, *C.W. Chen, W.C. Cheng,* Industrial Technology Research Institute, Taiwan, *C.C. Hsu*, National Taiwan University

An arc plasma jet under atmospheric pressure was studied. This plasma jet is able to generate stable plasma sustained by a DC pulsed power of 20 kHz ~ 40 kHz using nitrogen and clean dry air. A voltage probe and a current probe were used to characterize the voltage and current waveform of this plasma jet. The optical emission at this plasma jet downstream was monitored by an optical emission spectrometer. Multiple thermocouples were used to measure the downstream jet temperature. The current and voltage waveforms showed glow-to-arc-transition-like characteristics. It is found that the time-averaged current increases with the power input and is not sensitive to the flow rate. The peak current, however, increases as the applied power decreases and as the flow rate increases. The peak current remains below 1.0 A under high power and low flow rate conditions while reaches 3.0 A for low power and high flow operation regimes. It suggests that the peak current is not directly controlled by the amount of power input to the plasma. Optical diagnostics shows nitrogen molecular emissions dominate in nitrogen plasma jets. The nitrogen plasma jet temperature appears to be higher than the temperature of the air plasma jet as measured by the thermocouples at the jet downstream. The detailed discharge mechanism will be presented and its implications in materials processing will be discussed.

* PSTD Coburn-Winters Student Award Finalist

Nanomanufacturing Focus Topic
Room: 309 - Session NM+EM+PS+NS+NC-ThM

Printable Lithography and Processing
Moderator: D. Janes, Purdue University

8:00am **NM+EM+PS+NS+NC-ThM1 Techniques for Three Dimensional and Molecular Scale Nanofabrication**, *J. Rogers*, ***D. Shir***, University of Illinois, Urbana-Champaign **INVITED**

Progress in nanoscience and technology relies critically on the ability to build structures with nanometer dimensions. This talk describes unconventional lithographic methods based on (i) advanced forms of soft nanoimprint lithography for 2D patterning with resolution that extends to molecular (~1 nm) length scales, and (ii) conformable phase mask optics for single step formation of fully three dimensional (3D) nanostructures. The first method relies on optimized polymers for molds and mold materials that, together, enable lithographic fidelity at the ~1-2 nm scale, as demonstrated by the replication of relief structures defined by individual single walled carbon nanotubes with diameters down to ~0.7 nm. The use of this method to form alignment layers for liquid crystal devices illustrates a realistic application and a simple example of the broader notion of molded molecular structures for chemical and biological surface recognition. The second method exploits an unusual class of optical element – an elastomeric, sub-wavelength phase mask – in a contact mode exposure geometry to generate 3D structures in photopolymers and other materials in a single patterning step. Aspects such as the self-imaging, Talbot effect optics of this approach, its capabilities for creating periodic, aperiodic and quasi-crystalline 3D nanostructures and selected applications in microfluidics, laser fusion targets and photonic crystals will be discussed. This work was supported by the NSF and the Department of Energy.

8:40am **NM+EM+PS+NS+NC-ThM3 Preparation of 25-nm-spaced PdAu Metal Electrodes on Silicon by Direct Nanotransfer Printing**, ***S. Strobel***, *S. Harrer, G. Penso-Blanco, G. Scarpa, G. Abstreiter, P. Lugli,* Technische Universität München, Germany, *M. Tornow*, Technische Universität Braunschweig, Germany

Nanometer scale metallic contacts which can be directly deposited on planar substrates are of growing importance in view of future applications involving the integration of molecular electronics with current silicon technology. Here, a method which may provide well defined nanogap electrodes of predetermined spacing in a reproducible manner, without the need of sequential direct writing techniques, would be highly advantegous. We present a novel technique using direct high-resolution metal nanotransfer printing and demonstrate its capability to fabricate nanogap electrodes of predetermined spacing on a solid substrate such as silicon. The one-step transfer process is economical, simple and fast, and preserves the mold for manifold transfer. Using molecular beam epitaxy (MBE) a sandwich-like structure is grown with monolayer precision, comprising few nanometer thick GaAs layers embedded in AlGaAs. This structure is cleaved atomically flat perpendicular to the <110> crystallographic direction. Subsequently, the exposed GaAs layers are wet chemically etched thereby generating a 3D grating structure with nanometer-resolution at their edges. This structure serves as mold for nanotransfer printing: By coating the grating surface with a metallic thin film of PdAu/Ti (7/5 nm) and pressing the mold against a Si/SiO_2 substrate the patterned PdAu/Ti sandwich structure is directly transferred onto the surface. This one-step process does not require any flexible buffer layer or additional organic adhesion promoters. We report on a series of successful transfer experiments using different multi-line molds with varying aspect ratios and linewidths down to below 10 nm. In particular, we demonstrate electrically functional PdAu metal electrode pairs with separations down to 25 nm, featuring lead resistances of the order of kΩ and gap isolation in excess of 50 GΩ up to 2 Volts.

9:00am **NM+EM+PS+NS+NC-ThM4 Adhesion Enhancement using Plasma Processing in the Printing of Carbon-based and Organic Flexible Electronics**, ***D.R. Hines***, University of Maryland, *V.W. Ballarotto, C. Hull,* Laboratory for Physical Sciences, *G.S. Oehrlein, D.Y. Lee,* University of Maryland, *C.M. Stafford, C.L. Soles, E.K. Lin, J. Liu, J.-Y. Chung,* National Institute of Standards and Technology, *S.G. Walton, E.H. Lock*, US Naval Research Laboratory

High quality organic & carbon-based thin-film transistors (TFT) have been successfully fabricated onto plastic substrates using transfer printing. With this printing process, each device component (conducting electrodes, polymer dielectric layer and semiconductor layer) was printed using only pressure and temperature, eliminating all chemical processing on the plastic device substrates. Pentacene (Pn), poly(3-hexylthiophene) (P3HT), carbon nanotube mats (CNTM) and graphene TFTs were all fabricated on polyethylene terephthalate (PET) substrates. Bottom gate, bottom source/drain devices yielded mobilities of 0.237 cm^2/Vs for Pn and 0.04 cm^2/Vs for P3HT. Bottom-gate CNTM TFTs exhibited p-type behavior, mobilities of 13.7 cm^2/Vs, on/off ratio of 10^3 and minimal hysteresis. Top-gate graphene TFTs exhibited mobilities of $1.0x10^4$ cm^2/Vs for holes and $4x10^3$ cm^2/Vs for electrons. The organic TFT devices were fabricated using a variety of polymer dielectric layers including poly(hydroxystyrene) (PHS), polystyrene (PS), polycarbonate (PC) and poly(methylmethacrylate) (PMMA). The resulting TFTs showed little variation in mobility, but strong variation in threshold voltage for different dielectric layers. The transfer printing process relies primarily on differential adhesion for the assembly of both patterned and unpatterned films onto a common flexible, plastic substrate. It is a simple and robust process that is compatible with a wide range of materials. Plasma processing techniques are being adapted to control the surface energy of polymer and plastic surfaces in order to increase adhesion forces at the interface between polymer dielectric layers and plastic substrates. The printability and surface characterization of plasma treated polymer/plastic surfaces will be discussed. One goal of this work is to enable the incorporation of many different dielectric materials (including 10 test polymer dielectric films) and substrate materials (including 11 test plastic substrate sheets) into the fabrication of flexible electronics. This work partially supported by the Office of Naval Research and the Laboratory for Physical Sciences. *E.H. Lock, NRC/NRL Postdoctoral Research Associate.

9:20am **NM+EM+PS+NS+NC-ThM5 Fabrication of Microarrays with Nanoscale Chemical Contrast by Nanoimprint-Assisted Lift-Off**, ***A. Ruiz,*** JRC, European Commission, *C.A. Mills,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *A. Valsesia,* JRC, European Commission, *E. Martinez,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *P. Colpo,* JRC, European Commission, *J. Samitier,* Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *F. Rossi*, JRC, European Commission

The fabrication of ordered microstructures of colloidal crystals is increasingly attracting interest due to their potential applications as sensing, optical and photonic band-gap materials. Depending on the application (i.e. chemical or biochemical sensors, photonic chips), specific microstructured configurations of the colloidal crystal are needed. Most of the methodologies reported so far for the production of colloidal crystals are based on the directed self-assembly of micro or nanospheres, in which patterning and formation take place simultaneously in a template created beforehand, normally by the modification of the surface chemical or topographic properties. However, methods for patterning the colloidal film after it has been formed are scarce. The interest in such methods lies in the fact that they allow fine control over the microstructure of the colloidal film by selective removal of a single layer of close-packed nanospheres. Recent top-down approaches to the micropatterning of nano-beads are based on soft lithography lift-off processes using PDMS stamps. Removal of nano-beads strongly adhering to the substrate is however hard to realize and limitations related to the PDMS structural properties, i.e. deformation, appear. Normally, the beads have to be loosely attached so that bead transfer or removal is not inhibited. In this work, a new soft-lithographic method for micro-patterning nano-bead arrays, based on structured poly(methyl methacrylate) (PMMA) and using a nanoimprinter apparatus, is described. The properties of the PMMA, with respect to hardness and flexibility, are promising for resolving sub-micron patterns of nanoparticles. The use of the nanoimprinter allows careful control of the temperature and pressure during the contact-stripping operation; this ensures accurate removal of nanoparticles over large areas even when they are strongly attached to the substrate. Patterns of polystyrene nano-beads in several micro-scale configurations have been obtained using beads of different diameters (100 ~ 500 nm) and with different levels of adherence to the substrate. The micropatterning of nanobeads thus achieved has been then used to create surfaces with nanoscale chemical contrast inside the micro-patterns. Having structured regions separated by flat, unstructured regions is advantageous for many applications, such as sensing platforms for parallel detection or cell culture platforms for examining cell-surface interactions at the nanoscale.

9:40am **NM+EM+PS+NS+NC-ThM6 Inkless Deposition of Microparticles by Electrostatic Acceleration for Materials Processing**, *I. Eu, L. Musinski, T. Liu,* University of Michigan, *D. Morris,* ElectroDynamic Applications, Inc., ***J.M. Millunchick***, *B. Gilchrist, A.D. Gallimore*, University of Michigan

We have developed a particle accelerator that electro-statically charges nanometer- to micron-sized conductive particles that are then accelerated through grids with bias voltages up to roughly 10kV, allowing for the deposition of particles without using a carrier solution or "ink". By carefully controlling the energy of the particles, various regimes of materials processing may be achieved. For example, high energy high mass particles are expected to etch a substrate, while decreasing either the mass or velocity will result in deposition of the particles. A prototype device has been fabricated based on transporting the particles to and through an ultrafine "sieve" via back pressure and acoustic and/or mechanical vibration. The pressure and vibration moves the particles through the sieve apertures, allowing for electrostatic acceleration of the particles one at a time for maximum impulse. The experimental data shows a roughly Gaussian distribution of 50 micron Ag-coated glass spheres extracted at a mean electric field of about 1.9 MV/m with a standard deviation of approximately 0.4 MV/m. The data agrees well with the analytical model for required extraction fields determined using calculated Van der Waal's forces and a Lipshitz constant of 0.6 eV. The variance likely attributable to electrode surface roughness and manufacturing imperfections in particle shape. Initial feasibility tests have been conducted in which this system has been used to impact aluminum spheres of size 5-20 microns on glass slides. Scanning Electron Micrographs show that at a charging field of approximately 1.3 MV/m and an acceleration voltage of roughly 10kV, the glass slides are uniformly coated with individually isolated Al particles. The particle isolation and deposition control implies the potential for very high vertical and horizontal resolution in target applications. Now that the proof of concept has been established, we are scaling down the technology so that submicron particles may be deposited, with the long-term goal to deposit individual particles on the order of tens of nanometers.

10:40am **NM+EM+PS+NS+NC-ThM9 Plasma-Lithography Interactions for Advanced CMOS Manufacturing (45nm and Beyond)**, ***K. Kumar***, International Business Machines **INVITED**

The advent of 45nm saw the introduction of immersion lithography with up to 1.20 NA exposure conditions. The need for higher fidelity lithography printing gave rise to new resist, which in turn necessitated closer interactions with the plasma etch conditions. An overall synergistic model between litho and plasma etch was crucial for overall pattern fidelity. With the near horizons of the lithographic tooling window being limited to 1.35NA, and with EUV looking distant for prime time use, more emphasis is being placed on plasma etch pattern transfer for overall patterning fidelity. Added to scenario, is increased complexity in the form of "Double Expose Double Etch" which has helped increase the overall fidelity and density in the printing of the final structures in 32nm. In order to accomplish these tasks, engineering tools were developed or modified, that methodically studied the interactions between lithography and plasma etch. Strategy and results from Lithography – Plasma Etch interaction will be presented.

11:20am **NM+EM+PS+NS+NC-ThM11 Etching Development and Characterization for a Novel Nano-Imprint Lithography Technology**, ***J. Chiaroni***, *Y. Le Cunff, C. Charpin,* Minatec/Cea-Leti, France, *M.P. Clement,* St Microelect., France, *H. Denis,* Minatec/Cea-Leti, France, *G. Medico, M.L. Villani,* St Microelect., France, *N. Rochat, A. Fanton, L. Lachal, P. Brianceau, S. Barnola, F. Perrin, E. Vermande, P. Lavios,* Minatec/Cea-Leti, France, *N. Khusnatdinov, D. Labrake*, Molecular Imprint Inc., *J.P. Gouy,* Minatec/Cea-Leti, France, *P. Gubbini*, Molecular Imprint Inc.

Nano-Imprint Lithography (NIL) is one of the most promising candidates (ITRS road map 2007) to address the 32 nm node and below thanks to a high resolution capability (templates are manufactured with E-Beam Lithography), a compatibility with CMOS technology and a lower COO as a simpler technology. The method is based on stamping out patterns on a specific polymer and then transferring into the underneath materials. SFIL/R® is an innovative NIL technology proposed by Molecular Imprint Inc, which uses a stack of three materials: 1. TranSpinTM for initial planarization; 2. MonoMatTM in which pattern is printed; 3. SilSpinTM which planarizes MonoMatTM material. Then, two specific dry etching processes are required to generate the polymer mask: 1. Imprint features opening (SilSpinTM dry etch back with stop on MonoMatTM); 2. Polymers mask opening (TranSpinTM and MonoMatTM dry etching with high selectivity on SilSpinTM Hard Mask and CD control). One of the main challenges is to obtain a good etching selectivity between these three materials which are polymer based and very similar one to the other. SilSpinTM characterization has been performed with XPS and SIMS analysis in order to determine etching orientation. According to these results, imprint features opening was achieved with fluorinated chemistry (CHF3/O2/Ar) and Polymer mask opening with HBr/O2 or Cl2/O2 based chemistry. Study of plasma impact on SilSpinTM with XPS and FTIR analysis has shown a clear impact of chlorine due to its higher efficiency to break SilSpinTM characteristic bonding. So, HBr/O2 plasma has been preferred to perform the polymer mask opening. A Design Of Experiments was achieved with HBr/O2 based chemistry in order to determine the most effective input parameters and get the optimized selectivities. By adjusting HBr/O2 ratio and bias power, a selectivity of seven was obtained between SilSpinTM and pure organic materials, which is consider as high enough. Then, Vias and Lines applications were studied with cross section SEM and CD bias measurement. This work has been carried out within the frame of European program MEDEA+ 2T305 "«Fantastic».

11:40am **NM+EM+PS+NS+NC-ThM12 Influence of Polymer Structure on Dry Etch Behavior of Resists in Soft Lithography**, ***R.L. Bruce***, *F. Weilnboeck, S. Engelmann, T.C. Lin, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park, *B. Long, G. Willson,* University of Texas, Austin, *D.G. Nest, J.J. Vegh, D.B. Graves,* University of California, Berkeley, *A. Alizadeh*, GE Global Research Center

For the realization of sub-10 nm resolution, soft lithography alternatives to conventional photolithography are being considered. In soft lithography, the imprint material is used for pattern definition and also as a mask for pattern transfer into underlying layers. For successful nanoscale pattern transfer, a rational design of polymer resists and an atomistic understanding of plasma-polymer interactions are required. In this study, the effect of different species of the plasma (ions, UV, neutrals) on model polymers with distinct chemical structure (styrene-, acrylate-, methacrylate-, and vinylpyridine-based) was investigated. Model polymers were exposed to Ar and C_4F_8/Ar plasmas. Modification of the polymer surface was characterized using in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy (AFM). The effect of crosslinking and chain scission reactions, as well as oxygen containing functional groups, is considered. Mechanisms of plasma-polymer interactions for the different polymer structures are proposed. Finally, select polymers (poly(styrene), poly(α-methylstyrene), and poly(4-vinylpyridine)) were used as imprint materials, patterned, and plasma processed. The top and sidewall profiles and morphologies were examined by AFM and secondary electron microscopy before and after exposure. The importance of polymer structure and plasma species on pattern transfer in soft lithography is discussed.

Plasma Science and Technology
Room: 304 - Session PS1-ThM

Atmospheric Plasma Processing and Micro Plasmas
Moderator: J. Hopwood, Tufts University

8:00am **PS1-ThM1 Plasma Diagnostics in Microdischarges Using Laser Scattering**, ***S.G. Belostotskiy****, *V.M. Donnelly, D.J. Economou,* University of Houston, *N. Sadeghi*, Universite J. Fourier de Grenoble, France

Laser scattering experiments were performed in high pressure (100s of Torr) DC microdischarges operating in argon or nitrogen. Laser Thomson Scattering (LTS) and Rotational Raman Scattering were employed in a novel, backscattering, confocal configuration to measure important plasma parameters. LTS allows direct and simultaneous measurement of both electron density (n_e) and electron temperature (T_e). LTS experiments in microdischarges are challenging because of the low signal and excessive stray light. Measurements were performed at the center of the gap of a parallel plate slot-type microdischarge with plate separation of 600 microns. This location corresponded to the positive column of the DC microdischarge. For 50 mA current and over the pressure range of 300 – 700 Torr, measurements yielded $T_e = 0.9 \pm 0.3$ eV and $n_e = (6 \pm 3)\cdot 10^{13}$ cm^{-3}, in reasonable agreement with the predictions of a mathematical model. In order to obtain absolute values of the electron density, calibration of the Thomson scattered intensity was carried out using Raman scattering in nitrogen. This Rotational Raman spectroscopy was also employed to measure the gas temperature (T_g) in nitrogen DC microdischarges. Gas temperatures were determined by matching experimental spectra to synthetic spectra obtained by convolution of theoretical line intensities with the apparatus spectral resolution, with T_g as the adjustable parameter. Measurements were performed for a set of N_2 pressures (P = 400 – 600 Torr) and over the current range of 5 – 30 mA. In the center of the

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interelectrode gap, T_g changed from 450 ± 40 K at 5 mA to 740 ± 40 K at 30 mA. The gas temperature was nearly independent of pressure within the error of the experiment. Advantages and limitations of the laser scattering techniques employed will also be discussed.

8:20am **PS1-ThM2 The Effect of Excitation Frequency on Microplasmas**, ***J. Xue****, *J. Hopwood*, Tufts University

In the microwave band, higher excitation frequency is found to enhance microplasma generation. The microplasma is formed by a split-ring resonator (SRR) consisting of a half-wavelength microstrip transmission line formed into a ring with a micromachined discharge gap.[1] The SRR plasma can be operated from 0.1 to 760 Torr with less than 0.5 W of power in He and Ar. Typically, microplasmas have been generated with DC, AC, RF, and microwave power. One unanswered fundamental question, however, concerns the effect of frequency on microplasma generation. The excitation frequency of capacitively coupled plasma has been discussed by Surendra and Graves.[2] This early work suggests that plasma density scales as the square of the applied excitation frequency. That work focused on large-scale plasma at low pressure and the excitation frequency was limited to less than 120 MHz. This paper presents plasma impedance analysis of three microplasmas operating at excitation frequencies of 450 MHz, 900 MHz, and 1.8 GHz. The electron density and sheath capacitance of the microdischarges are extracted from the plasma impedance. Experimentally, these three SRR's are fabricated on microwave laminate (Rogers, RT/Duroid 6010LM) with identical microstrip widths (1 mm) and discharge gaps (200 µm). The radii of the rings are scaled by 1/f and the smallest radius is 5mm at 1.8 GHz. To determine the plasma impedance, the microwave reflection coefficient is measured as a function of frequency while maintaining a constant microwave power absorbed by the plasma. Using the method in Ref. 1, the microplasma impedance is found by fitting the theoretical microwave reflection coefficient to the measured reflection coefficient. The results show that microplasmas generated by higher frequency resonators have a lower plasma resistance. The extracted electron densities in argon microplasma at 760 Torr are estimated as 2.4, 6.0, and 8×10^{13} cm^{-3} for the 450 MHz, 900 MHz, and 1.8 GHz SRR, respectively. The imaginary part of the plasma impedance provides a model of the plasma sheath capacitance. This data shows a diminishing sheath impedance at high frequency which is responsible for improved electron density.

[1] F. Iza and J. Hopwood, Plasma Sources Sci. Technol. 14, 397 (2005).
[2] M. Surendra and D. B. Graves, Appl. Phys. Lett. 59, 2091 (1991).

8:40am **PS1-ThM3 Generations, Characterizations and Applications of Microplasmas Operated in Atmospheric Gases and Artificial Media**, ***K. Tachibana***, Kyoto University, Japan **INVITED**

Microplasmas of sub-millimeter to micrometer scales can be operated in high pressure gases or high density media with a choice of single or integrated usage. The electron density n_e of a typical microplasma lies in the range of 10^{12} to 10^{15} cm^{-3} even though the ionization degree is rather small. As for the electron temperature T_e, it shows non-equilibrium natures inherently due to the short residence time in small space or short duration of pulsed discharge in the generation. Taking the advantage of these non-equilibrium properties, microplasmas have been applied to various purposes such as material syntheses, surface treatments, environmental and biomedical issues, etc. In this talk, I would like to introduce some examples of new schemes of microplasma sources with their characterizations by various diagnostic methods; we have been applying optical emission spectroscopy (OES), laser absorption spectroscopy (LAS), and laser-induced fluorescence spectroscopy (LIF) for the measurements of excited and ionized species as well as THz time-domain spectroscopy (TDS) and infrared CO_2 laser heterodyne interferemetry for plasma parameters. In addition to the microplasma generation in usual gas phase, we have been trying to use atmospheric gases with liquid vapors (mists) and aqueous solutions with micro bubbles as artificial media of microplasmas under controlled (characterized) conditions. As one of the examples, by using a fabric electrode assembly weaved with insulated wires, we have succeeded in the generation of microplasmas in H_2 or O_2 bubbles produced underwater by electrolysis. Those results will be explained together with some examples of their potential applications.

9:20am **PS1-ThM5 Atmospheric Dielectric Barrier Glow Discharges at High Overvoltage**, ***B.D. Schultz***, *A.R. Martin, M.A. Ray, G.E. McGuire, W.M. Hooke*, International Technology Center

Atmospheric dielectric barrier plasma glow discharges in pure nitrogen gas have been generated under overvoltage conditions produced with a custom high voltage source. A voltage rise time of 25 ns at 20-30kV is readily achieved by the source and is sufficient to create overvoltage conditions in excess of three times the DC breakdown voltage of nitrogen. These large overvoltage conditions occur because the rise-times required to achieve peak voltage are shorter than the lag time between the pulse crossing the threshold voltage and the onset of a discharge. Overvoltage conditions prior to discharge have been predicted to produce significantly higher average electron energies in the discharge and to produce high instantaneous power densities. Experimentally current densities have been achieved well in excess of 10 A/cm^2 for homogeneous glow discharges of pure nitrogen gas at atmospheric pressure with total pulse currents of 1 kiloamp having been obtained. The overvoltage potential on the electrodes enables manipulation of the reduced electric field, but additional control can also be garnered through increases in the gas temperature and/or decreases in the chamber pressure along with the applied overvoltage. This paper will emphasize the correlation between the overvoltage conditions, the dielectric material properties, temperature, and small deviations in pressure to the electrical charge transfer, optical properties, and propagation mechanisms of the glow discharge. This work was supported in part by ARL and AFRL.

9:40am **PS1-ThM6 Decoloration of Organic Dyes by Bipolar Pulsed Electrical Discharge in Aqueous Solution**, ***Š. Potocký***, *N. Saito, O. Takai*, Nagoya University, Japan

During recent years plasma systems in liquid have become a topical interest. They open new possibilities in wastewater treatment. Those systems are able to produce highly active species which finally results in conversion of the organic to innocuous materials. Nevertheless, the drawback of such system meets with the requirement of very high voltage for sustaining the plasma discharge and relatively low energy efficiency. Another important process is the erosion of the electrodes that limits the operating lifetime or leads to the pollution of treated water with metal particles released from the electrodes. We demonstrate operation of solution plasma process under relatively low discharge voltage (below 4 kV) and two different plasma regimes with pulse energies in mJ range using a high frequency bipolar pulsed DC power supply. It can be operated up to the repetition frequency of 30 kHz with a pulse width range from 2 µs to 10 µs and a maximum voltage and current of ±6 kV and 7 A, respectively. The oxidative decoloration of organic dyes by the bipolar pulsed discharge plasma between needle-to-needle electrodes in water solution has been investigated in two discharge modes: (i) corona, (ii) spark/streamer mode. Ratio between H-alpha and hydroxyl radical emission line intensity differ by two orders of magnitude in those two modes even for high value of solution conductivity (1 mS/cm) which is close to typical value of a wastewater. The current-voltage characteristics of the system together with an optical emission spectroscopy of plasma discharge were used to characterize regimes of plasma discharge operation. Analysis of generated hydrogen peroxide concentration by colorimetric method using titanium reagent and the absorption spectroscopy was performed. Measurement of electrodes erosion and metal concentration (by inductively coupled plasma mass spectroscopy) due to solution plasma process was also carried out indicating obvious difference in two modes of plasma discharge operation.

10:40am **PS1-ThM9 Surface Modification of Ultra High Molecular Weight (UHMW) Polyethylene Films Using Atmospheric Pressure Dielectric Barrier Discharges**, ***D.D. Pappas***, *K.E. Strawhecker, A.A. Bujanda*, United States Army Research Laboratory

In this work, dielectric barrier discharge (DBD) plasmas, operating in nitrogen, air and helium-oxygen at atmospheric pressure, are used to modify the surface properties of ultra high molecular weight polyethylene films. The imposed changes of the hydrophilicity, chemical composition and roughness of the surface appear to have a dependence on the DBD operating parameters such as processing duration and discharge power as well as the nature of the gas being used for the plasma treatment. Contact angle and X-ray photoelectron spectroscopy (XPS) data reveal that in all cases the plasma exposed surfaces exhibit improved wettability that can be attributed to the mild oxidation of polyethylene as confirmed by XPS analysis. Atomic force microscopy (AFM) results show that longer processing duration and higher oxygen concentration are key for increased surface roughness, a factor affecting the adhesion properties of the film. Standard lap-shear evaluations reveal that plasma treatments may lead to significant increases in the bond strength of polymer films and metallic/polymeric substrates and changes in modes (adhesive vs. cohesive) and loci of failure. The plasma treatments increase the mechanical interlocking and frictional energy dissipation effects when bonded to a substrate. Changes in other mechanical properties are also investigated. Most importantly, this uniform modification occurs within a few seconds of exposure, time comparable to continuous on-line industrial processing.

* PSTD Coburn-Winters Student Award Finalist

11:00am **PS1-ThM10 The Discharge Characteristics of an Industrial Scale Atmospheric Pressure Uniform Plasma Processing System**, ***W. Graham****, D. Della Croce, L. Schaper,* Queens University Belfast, Northern Ireland, *L. O'Neill, A.M. Hynes*, Dow Corning Plasma Solutions, Ireland

Time and space-resolved electrical, optical and imaging characterisation of a commercial, 1800cm^2 atmospheric pressure plasma system, operating with polymer film is reported. . The system is based on a dielectric barrier discharge operated in air with flowing helium. The system is optimized for plasma treatment, rather than the physical appearance of the plasma. The Dow Corning Plasma Solutions LabLine™ system establishes discharges in two back to back, identical 340mm x 300mm transparent, electrode structures each with an inter-electrode gap of 5mm. The driving power supply produces a sinusoidal voltage, of up to 20 kV peak to peak, at frequencies of around 20 kHz. This is applied to the two internal electrodes. The outer electrodes are grounded. Helium is introduced from the top of the electrodes. Polyethylene Terephthalate (PET) polymer film could be suspended in the centre of the electrode gap, parallel to the glass dielectrics. Standard high voltage and current measurement techniques were used monitor the voltage applied to the electrodes and the current (Id) drawn through the power cable to the electrode assembly. A fast photomultiplier tube was used to measure the temporally resolved emission from the discharge while the spatially and temporally resolved behaviour of the discharge was studied by imaging the electrodes and the electrode gap onto a gated ICCD. The imaging indicates that with or without polymer film present, static or moving, radially uniform discharges, persisting for a few microseconds, are consistently created at the same phases of the applied voltage. The number of discharges increases with increasing input power and hence applied voltage. The structure of the discharge emission is suggestive of that of an atmospheric pressure being most intense at the cathode and showing evidence of a dark space and much less intense emission beyond that. At higher input powers, when the applied voltage considerably exceeds the initial breakdown voltage, these discharges occur so frequently that they sustain and enhance these structured discharges for periods of up to 25 µs. In the presence of the polymer film the discharge was generally more intense in the region occupied by the film and always produced emission between the polymer and the cathode. The authors wish to thank Dr. D. Dowling and B. Twomey of U.C. D. for their support and assistance and gratefully acknowledge EPSRC and Dow Corning support for of D. D. C.

11:20am **PS1-ThM11 Influence of Air and Water Vapour Contaminations on the Atmospheric Pressure PECVD of Fluorocarbon Thin Films**, ***F. Fanelli****,* Univeristy of Bari, Italy, *R. d'Agostino, F. Fracassi*, University of Bari, Italy

Low pressure plasma-enhanced chemical vapour deposition (PECVD) of fluorocarbon films has been extensively studied in the last decades. Very recently atmospheric pressure dielectric barrier discharges (DBDs) have been addressed as an attractive route towards the deposition of fluoropolymers, nevertheless, the utilization of this approach is still a challenge. Research efforts should be devoted to evaluate if DBDs can actually be advantageous compared to low pressure plasmas; for this purpose, besides the fundamental investigation of fluorocarbons fed DBDs, it is also important to gain insights into the influence of contaminants such as air and water vapour. The presence of these contaminants into the atmospheric pressure reactor could have, in fact, serious detrimental effects on the overall deposition process because it might result in a drastic decrease of the F/C ratio of the films, in the uptake of oxygen and nitrogen as well as in deposition rate reduction. On the other hand, the knowledge of the highest level of contamination compatible with an acceptable process performance and consequently the possibility of depositing fluoropolymers in “contaminated” environments could allow to reduce the cost of plasma processes and reactors. For these reasons we decided to evaluate the influence of air and water vapour contaminations on the PECVD of fluoropolymers in atmospheric pressure cold plasmas. Controlled amounts of air and water vapour have been added to a DBD fed with argon-hexafluoropropene (Ar-C_3F_6). The discharge regime has been clarified by electrical measurements, while film characteristics have been studied by FTIR, XPS, WCA measurements and SEM. Gas phase has been investigated by optical emission spectroscopy and the stable species contained in the gas effluent have been analyzed using gas chromatography coupled with mass spectrometry, in order to have indications on the reactive fragments generated inside the discharge. The results obtained in this work show that Ar-C_3F_6 DBDs allow to deposit coatings with a deposition rate of 56 nm/min and a XPS F/C ratio of 1.7. Contaminants addition causes a slight variation of the F/C ratio and a decrease of the deposition rate. In particular, if the [Air]/[C_3F_6] and [H_2O]/[C_3F_6] ratios in the feed are kept below 0.25 and 0.125, respectively, the variation of the F/C ratio is negligible and the deposition rate remains higher than 45 nm/min.

11:40am **PS1-ThM12 Characterization of Atmospheric Pressure Plasma with Arc-free and Antistatic Plate for Flat Panel Displays, Solar Cells, Semiconductor, and Nano-biology Processing**, *K.H. Lee, H.R. Lee, Y.J. Park,* ***S.I. Jun***, PSM America Inc.

We have characterized the parametric and functional properties of Atmospheric Pressure (AP) Plasma System with newly designed Arc-free and Antistatic Plate to provide uniform and arc-free AP plasma on substrates such as glass, wafers, and any flexible substrates for improving surface treatments. The AP Plasma System showed very highly efficient capabilities of removing organic contaminants for flat panel displays, semiconductor, and solar cell processing with very high throughputs and very low running coat provided by in-line layouts and usage of CDA (cold dry air) not using expensive gas such as helium. The AP treated substrates and thin films showed drastic lowering of the contact angles; 43 degree to 5 degree for bare glass substrate and 70 degree to 8 degree for ITO thin films. The etch rate non-uniformity of ITO films on 730x920mm glass substrate was improved from 8.8% to 7.5% after AP Plasma treatment with the Arc-free and Antistatic Plate. Besides these conventional applications of AP Plasma, we have proposed newly emerging applications, nanobiotechnologies. The AP Plasma System showed much improved performances in (1) direct contact with living tissue, (2) wound treatment with living tissue sterilization, (3) promoting blood coagulation, (4) skin flora sterilization, and (5) treatment of human melanoma, macrophages, and leishmania major promastigote cell line.

Plasma Science and Technology
Room: 306 - Session PS2-ThM

Plasma Modeling
Moderator: D.J. Economou, University of Houston

8:00am **PS2-ThM1 Wave and Electrostatic Coupling in Dual Frequency Frequency Capacitively Coupled Plasmas Utilizing a Full Maxwell Solver***, ***Y. Yang****, M.J. Kushner*, Iowa State University

Dual frequency, capacitively coupled plasma (DF-CCP) tools are being developed for etching in microelectronics fabrication with the goal of separately controlling the production of etch precursors and ion energy delivered to the wafer. These tools typically use a high frequency (10s to 100s MHz) to sustain the plasma and a low frequency (a few to 10 MHz) for ion acceleration. With an increase in both the high frequency and wafer size, electromagnetic wave effects (i.e., propagation, constructive and destructive interference) can affect the spatial distribution of power deposition and reactive fluxes to the wafer. These effects are difficult to computationally address due to the coupling between electromagnetic and electrostatic fields, the latter of which is responsible for the formation of the sheath. In this talk, we discuss results from a computational investigation of high frequency effects in DF-CCPs. A 2-dimensional Maxwell equation solver utilizing Finite Difference-Time Domain techniques capable of resolving wave and electrostatic effects in arbitrary geometries was developed and incorporated into the Hybrid Plasma Equipment Model. To capture the high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. The method of solution will be discussed and validation will be made by comparison with experiments for single frequency excitation. Experimental trends of the transitioning of the plasma density from flat to edge to center peaked (corresponding to electrostatic, skin depth and wave dominated regimes) with increasing frequency are captured by the model. Results from a parametric investigation of DF-CCPs (LF $\leq$ 10 MHz, HF $\geq$ 50 MHz) in polymerizing gas mixtures will also be discussed. Assessments will be made of the changes in power deposition and electron impact ionization profiles as a function of frequency, the location of power coupling and intervening materials.

*Work supported by the Semiconductor Research Corp., Tokyo Electron Ltd. and Applied Materials Inc.

8:20am **PS2-ThM2 Three-Dimensional Modeling of Capacitively-Coupled Plasmas with Asymmetric Reactor Elements**, ***J.A. Kenney****, S. Rauf, K. Collins*, Applied Materials, Inc.

Much of the focus in past plasma uniformity studies has been on center-to-edge non-uniformity, which can generally be addressed through careful plasma reactor design and process optimization. As plasma processing uniformity requirements grow more stringent, there is an increasing emphasis on the characterization of asymmetric reactor elements which may give rise to azimuthal non-uniformities. The complexity of these systems can make experimental analysis of isolated components difficult, however, which has provided an impetus for the development of a three-dimensional fluid plasma model. Herein, we describe the model and its use in the

investigation of several azimuthally asymmetric elements in typical plasma processing reactors. In our three-dimensional model, charged species densities are computed by solving continuity equations for all species using the drift-diffusion approximation. The coupled set of charged species continuity equations and Poisson equation, which governs the electrostatic fields, is solved implicitly in time. The electron temperature is determined by solving the electron energy equation. The model also includes the full set of Maxwell equations in their potential formulation, Kirchhoff equations for the external circuit, and continuity equations for neutral species, along with non-uniform mesh generation to better resolve regions of interest. Using this model, we have investigated several azimuthally asymmetric components with the potential to perturb the plasma density, ion flux at the wafer, and electric fields. Ar is the feed gas in all simulations. For 13.56 MHz capacitively coupled plasma (CCP) discharges with peak plasma densities near the electrode edges, asymmetric elements include discontinuities of various sizes and locations in the reactor wall (e.g., diagnostic ports, slit valve) as well as the presence of off-axis circular plates surrounding the lower electrode. For 162 MHz CCP discharges with densities typically peaking in the reactor center, the impact of electrode planes aligned off-normal to each other is investigated, for several degrees of tilting and at different electrode gaps. Fourier analysis is used as appropriate to quantify the degree of perturbation induced by each asymmetric component.

8:40am **PS2-ThM3 Flow-Plasma Interactions in Plasma Etching: A 3-Dimensional Computational Investigation**, ***A. Balakrishna**, S. Rauf, K. Collins*, Applied Materials, Inc.

Plasma etching is a complicated process where plasma dynamics, gas and surface chemistry, and fluid flow all have significant influence on the processing results. Flow effects in commercial plasma etching reactors cannot be accurately captured in 2D models or 3D plasma-only models. While 3D flow-only models have been used to evaluate the redistribution of important plasma species and to suggest hardware improvements, this approach limits the understanding of the influence of fluid flow on the plasma. In particular, hardware changes made to improve flow symmetry impact plasma distribution, and vice versa. We have developed an integrated 3D flow and plasma model to enable this concurrent optimization. In this model, the Navier-Stokes equations in cylindrical coordinates were solved using a finite volume method. The equations were discretized using flux balances on each computational cell. The pressure distribution was computed using the SIMPLE method,[2] which corrects the flow and pressure fields to fulfill mass conservation. The calculated flow distribution was passed to the plasma model, which includes the full set of Maxwell equations in their potential formulation. The vector potential is solved in the frequency domain after each cycle, with current sources computed using results from the previous cycle. The coupled set of equations governing the scalar potential and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron energy equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. The 3D fluid-plasma model was used to understand the operation of capacitively coupled plasmas operating at 13.56 and 160 MHz in this paper. Both electropositive (Ar) and electronegative (O2) gases were considered. Comparison of the solutions with and without fluid flow interaction allowed us to separate the effects of flow and plasma on species distribution in the chamber. At sufficiently high flow rates, azimuthal flow non-uniformities were reflected in the plasma species distributions.

[1]J. Kenney, S. Rauf and K. Collins, AVS 2008.

[2]S.V. Patankar and D.B. Spalding, Int. J. Heat Mass Transfer, vol. 15, pp. 551-559 (1972).

9:00am **PS2-ThM4 Modeling of Micro-Scale Si Etching under Plasma Molding in 2f-CCP in SF_6/O_2**, ***F. Hamaoka**, T. Yagisawa, T. Makabe*, Keio University, Japan

Reactive ion etching (RIE) used for fabricating a nanometer-scale element of the semiconductor device has been applied to the process of a micro-scale etching in micro-electro-mechanical system (MEMS). Plasma molding is one of the important issues in micro-scale etching with several tens or hundreds of micrometers in width and depth.[1] In our previous study, the influence of the ion transport under the distorted sheath potential, i.e., plasma molding, on the anisotropic Si etching was numerically investigated without considering the neutral reaction.[2] In addition to the effect of ions, we developed the gas-phase and surface model for Deep-RIE of Si in a 2f-CCP in SF_6/O_2 under competition between Si etching and passivation layer formation, including the effect of plasma molding.[3] These investigations imply that the ions incident on the wafer under the distorted sheath potential by plasma molding remove the passivation (SiO_xF_y) layer on the sidewall and bottom corner, suppressing etch anisotropy. In this study, we numerically investigate the feature profile evolution of Deep Si etching under the presence of the plasma molding in 2f-CCP in SF_6/O_2 as functions of gas mixture and pressure with different widths of micro-scale pattern. The sidewall etching is suppressed drastically with increasing the oxygen mixture ratio due to forming the passivation layer by oxygen radicals on the Si surface. In SF_6/O_2(50%) at 300 mTorr, the etching profile of 250μm-wide-pattern is distorted especially at the bottom corner because of the excess ions with radially distorted angular distribution by plasma molding. On the other hand, at 100 mTorr, the etching profile at the bottom is flattened by chemical effect at the center due to the smaller flux of $O(^3P)$ than that at 300 mTorr; however, the sidewall etching occurs slightly. We will also discuss the etching profile with different pattern widths under plasma molding in 2f-CCP in SF_6/O_2.

[1] D. Kim and D. J. Economou, IEEE. Trans. Plasma Sci., vol. 30, no. 5, pp. 2048–2058, 2002.

[2] F. Hamaoka, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys., vol. 46, no. 5A, pp. 3059-3065, 2007.

[3] F. Hamaoka, T. Yagisawa, and T. Makabe, IEEE Trans. Plasma Sci., vol. 35, no. 5, pp. 1350-1358, 2007.

9:20am **PS2-ThM5 Computer Simulations of Processing Plasmas**, ***A. Bogaerts***, University of Antwerp, Belgium **INVITED**

In this talk, an overview will be given of different modeling activities going on in our research group, for the aim of improving the applications of processing plasmas. There exist several approaches in literature to model gas discharge plasmas, each with their own advantages and disadvantages. In this presentation, several examples will be given of plasma modeling activities going on in our research group, to illustrate the capabilities and limitations of the various modeling approaches. More specifically, the following topics will be presented: Fluid modeling for describing the detailed plasma chemistry, leading to nanoparticle formation in dusty silane and acetylene discharges; Fluid modeling for describing dielectric barrier discharges (DBDs), used e.g., for surface treatment, but also for biomedical or environmental applications; PIC-MC modeling for describing magnetron discharges, for sputter-deposition applications of thin films; Hybrid MC-fluid modeling for describing inductively coupled plasmas (used for etching applications in the microelectronics industry) and glow discharges (used for analytical spectrochemistry applications). In each case, both the model and the type of discharge will be briefly outlined, and typical calculation results will be presented. Furthermore, it will be demonstrated why this particular modeling approach is most suitable for this application. Beside these computer models for the plasma itself, it is also of great interest to simulate the interaction between the plasma and the walls of the plasma reactor, because (i) this defines the boundary conditions of the plasma simulations, and (ii) it is essential for important applications such as thin film deposition and surface etching. For this purpose, we apply molecular dynamics (MD) simulations. The capabilities and limitations of MD simulations will be illustrated for the case of plasma deposition of nanostructured carbon materials (nanocrystalline diamond thin films or carbon nanotubes).

10:40am **PS2-ThM9 Simulation of Profile Evolution in Shallow Trench Formation by Plasma Etching**, ***J. Hoang****, *J.P. Chang*, University of California, Los Angeles

In this work, a Monte Carlo based feature scale model was developed to accurately portray the profile evolution during shallow trench isolation etch (STIE) in chlorine based plasmas. A novel surface representation eliminates the artificial surface flux fluctuations due to the highly sloped sidewall features under simulation and the discrete cell nature of the simulation domain. It also enables a precise calculation of the surface normal, which dictates the trajectory of the reflected reactive species that control the profile evolution. The number of particles simulated is estimated from the depth and width of the etched profiles determined by scanning electron microscopy (SEM), with the assumption that the etch processes occur at high neutral-to-ion flux ratios. Through a set of carefully planned design of experiments (DOE) in which the effects of plasma density and plasma chemistry were assessed, the model was shown to accurately predict key features of STIE profiles, including microtrenching, mask faceting, and sidewall tapering, as a result of changing neutral-to-ion ratio, the mean ion energy, ion energy and/or angle distribution function. A two-dimensional numerical fluid model was developed to investigate the dual-coil and dual-feed reactor design on the radial profiles of plasma species, namely etch products and positive ions. The dual-coil parameter was determined to be effective in tailoring the radial ion flux profile at pressures higher than 20 mT, while the dual-feed parameter was shown to alter the etch product transport in the convection-dominant flow regime. Coupling of the reactor scale model to the feature scale model allowed investigation of subtle yet important changes in the etched feature profile from the center to the edge of the wafer. This hybrid model suggests that the radial decrease in the etch depth from wafer center to edge, seen from a set of DOE, is caused by an inherent net neutral-to-ion ratio decrease. In addition, the increase in the silicon sidewall angle from wafer center to edge can be qualitatively explained by a decrease in the concentration of the etch products. To study

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* PSTD Coburn-Winters Student Award Finalist

the local variations at the die/meso scale, the simulation domain is expanded to study the effects of etch product distributions at the die level.

11:00am **PS2-ThM10 Investigation of Micro-Trenching, Bowing and Charge Accumulation on Mask using a Dry Etching Simulator Designed for Low-Pressure High-Density Plasma**, ***J. Saussac**, J. Margot,* Université de Montréal, Canada*, M. Chaker*, INRS-Energie, Matériaux et Télécommunications, Canada

The development of new sub-micron technologies requires a fundamental understanding of device fabrication processes in order to be able to push the technology to its limits. In particular, in the context of plasma etching, the quality of patterning critically depends upon a number of plasma characteristics and on the surface reactivity with respect to the plasma species. Numerical simulation is of great interest for providing insights into the physics underlying various processes and to indentify the etching control mechanism. We developed a cellular Monte-Carlo-based dry etching simulator designed for low-pressure high-density plasma. The simulation code has been validated for various experimental profiles, namely Si, SiO_2, $SrTiO_3$ and Pt thin films etched in Ar and Ar/Cl_2 plasmas. The observations of both micro-trenching, due to ion scattering on sidewalls, and bowing, due to lateral etching, are well reproduced for various profile widths from 4 µm to 500 nm, which validates the simulation approach. We also investigated the effect of electrical mask charging during Pt etching in Ar plasma. Assuming an electrical field near the mask surface through positive charge accumulation yields the angular deviation of impacting ions. It will be shown that the etching profile obtained by our simulation is in good agreement with that observed from scanning electron microscopy.

11:20am **PS2-ThM11 Atomic-Scale Numerical Simulations of Surface Reactions in Carbon-Based Thin Film Deposition Processes**, ***Y. Murakami**, S. Horiguchi,* CANON ANELVA CORPORATION Japan*, S. Hamaguchi*, Osaka University, Japan

Diamond-like carbon (DLC) films have attracted much attention in the coating technology community. In our experiments, DLC films as protection layers for data recoding disks have been developed. Characteristics of DLC films are generally determined by the amount of sp^3 hybridized bonds present in the films, which may be controlled by hydrocarbon species and its injection energy used for the deposition process. Various mechanisms of formation of sp^3 hybridized bonds in DLC films have been proposed,[1] but some details are yet to be understood better. In this work, in an attempt to establish a high quality DLC deposition process, we have used molecular dynamics (MD) simulations to understand interaction between carbon containing gaseous radical species and an amorphous carbon (α-C) surface. Especially focused in this work are interactions of incoming CH_3 and CH species with an unhydrogenated α-C surface. The interatomic potential functions used in this study are the same as those used in Ref.2. In simulations charge-neutral CH_3 or CH radical species are injected 300 times ($7.5\times10^{15}cm^{-2}$ dose) normally into the top surface of the substrate with incident energies in the range from 2eV to 50eV. The substrate temperature is kept at room temperature (300K) at the beginning of every injection. In our results, it is found that the sticking probabilities of both C and H atoms of the incoming to the substrate surface depend on the incident energy. It is also shown that the sticking probability of a CH radical is higher than that of a CH_3 radical in the entire energy range. It is due to the fact that a CH radical has more dangling bonds that energetically favor forming complete bonds with C atoms of the substrate. The fraction of sp^3 hybridization bonds is also found to be higher in the case of CH_3 injections. This indicates that, with the availability of more hydrogen atoms, a carbon atom tends to form more diamond-like structures. These results may be used for the development of deposition processes for high quality DLC films.

[1] J. Robertson, Materials Science and Engineering, R37 (2002) 129.

[2] H. Yamada and S. Hamaguchi, Plasma Phys. Control. Fusion 47 (2005) A11.

11:40am **PS2-ThM12 Coupling Reaction Kinetics of Gas Phase, Reactor Wall, and Wafer Surface in C_4F_8 and SF_6 Plasmas with Global Models**, ***G. Kokkoris**, E. Gogolides,* NCSR Demokritos, Institute of Microelectronics, Greece*, A. Goodyear, M. Cooke*, Oxford Instruments Plasma Technology, UK

C_4F_8 plasma has been used for dielectric etching in microelectronics and, in combination with SF_6 plasma, for deep Si etching during the Bosch process in the area of micro-electro-mechanical systems fabrication. C_4F_8 is also met in plasma enhanced chemical vapor deposition of fluorocarbon (fc) films. Several models for C_4F_8 plasmas have been reported,[1] while there is a lack of models for SF_6 plasmas[2] in low pressure conditions. None of the models has focused on the interaction of the bulk phase with the reactor surfaces. The importance of the interaction increases as the constraints for manufacturing become stricter; it can affect the reproducibility of the process.[3] In this work, a 0D or global type model for C_4F_8 and SF_6 plasmas is formulated and is combined with a surface reaction model. The combined model, not only takes into account the effect of the surface reactions on the species densities in the bulk, but also allows the calculation of derived outputs which extend the potential experimental measurements for the validation of global models. In particular, it allows the calculation of a) the pressure change after the ignition of the discharge which links to the degree of dissociation of the parent gas, b) the effective sticking coefficients of the species which signify the net consumption of the species on the reactor surfaces and are the values measured in the experiments, and c) the deposition rate and the ratio of F/C of the fc film (C_4F_8 case), which can affect e.g. the SiO_2 etching selectivity over Si and the dielectric constant of the film. The results of the combined model compare well with measurements of pressure change and densities of F atoms, CF_x radicals, and ion flux versus power and pressure in an inductively coupled plasma reactor. For C_4F_8, the parent gas is vastly dissociated, CF_4 dominates after 1000 W, and production of CF_3 at the reactor walls is predicted. For SF_6, the loading phenomenon during Si etching is predicted.

[1] G. I. Font, W. L. Morgan, and G. Mennenga, J. Appl. Phys. 91, 3530-3538 (2002).

[2] C. Riccardi, R. Barni, F. De Colle, and M. Fontanesi, IEEE Trans. Plasma Sci. 28, 278-287 (2000).

[3] G. Cunge, B. Pelissier, O. Joubert, R. Ramos, and C. Maurice, Plasma Sources Sci. Technol. 14, 599-609 (2005).

Plasma Science and Technology
Room: 304 - Session PS1-ThA

Plasma Diagnostics, Sensors, and Control II
Moderator: V.M. Donnelly, University of Houston

2:00pm **PS1-ThA1 Spatial Density Distribution of Low-energy Electrons in a 2f-CCP by Laser Absorption and Optical Emission Spectroscopy**, ***T. Ohba***, KEIO University, Japan, *T. Kitajima,* National Defense Academy of Japan, *T. Makabe*, KEIO University, Japan

Optical emission spectroscopy (OES) is widely used as the tool of plasma diagnostics and plasma characteristics. The OES is restricted to the phenomena caused by higher energy electrons over the threshold of the electronic excitation of the target molecule mostly greater than ~10 eV, while the mean energy of electrons in a low-temperature radio frequency plasma is typically 3-5 eV in the bulk plasma, A simple in-situ method to determine spatiotemporally resolved transport of low energy electrons in a two-frequency capacitively coupled plasma (2f-CCP) is presented by using OES and laser absorption spectroscopy in pure Ar.[1] The method employs the long-lived metastable atom $Ar(1s_5)$ and short-lived excited $Ar(2p_9)$. Due to the large cross section of metastable atoms with electrons,[2] the net excitation rate of $Ar(2p_9)$ obtained by OES is expressed as a function of the electron density at the peak energy ~3.3 eV and the metastable density. The spatiotemporal measurement of the electron density distribution with energy of ~3 eV is demonstrated in a typical condition in a 2f-CCP, driven at 100 MHz and biased at 500 kHz in pure Ar at 25, 50 and 100 mTorr. The density shows almost no dependence on time in the bulk plasma and has a sharp peak in the sheath in front of the bias electrode at higher pressure. The influence of photon reabsorption will be further discussed.

[1]M. Ishimaru, T. Ohba, T. Ohmori, T. Yagisawa, T. Kitajima and T. Makabe, Diagnostics for low-energy electrons in a two-frequency capacitively coupled plasma in Ar , Appl. Phys. Lett. 92, 071501 (2008)

[2]A. A. Mityureva and V. V. Smirnov, Opt. Spectrosc. 97, 508 (2004).

2:20pm **PS1-ThA2 Time-Resolved Absorption Spectroscopy with LEDs as Light Source: Application to Etching Plasma Monitoring**, ***G. Cunge***, *D. Vempaire, M. Touzeau, N. Sadeghi*, LTM-CNRS, France

Broad band absorption spectroscopy is widely used to measure the concentration of radicals, which is important to understand the physical chemistry of many plasmas. We show that it is possible to increase significantly the sensitivity of this technique and to perform time-resolved measurement by using Light Emitting Diodes (LEDs) as a light source. This is obtained thanks to the high stability of the LED intensity. By modulating the LED current and using a lock-in amplifier for light detection, it is possible to get rid of the plasma emission, which greatly enhances the reliability of the absorption spectroscopy technique in reactive plasmas. In particular, wavelength dependent absorption cross section can be measured without any distortion, inherent to baseline fluctuations when using other light sources such as Xe arcs. This is particularly important when the species absorbs over a broad band continuum. Finally, we show that it is possible to achieve time resolved measurements of radical density decay in the afterglow of pulsed discharges, giving insight into the gas phase and surface loss processes of these radicals. The method is applied to study radical loss kinetics in BCl3 and SiCl4 based high density plasmas. We concluded that UV absorption with LED is a new and powerful plasma diagnostics, which allows detecting several radicals with a small and low cost equipment, and which may be used for real time process monitoring applications.

2:40pm **PS1-ThA3 Spatio-temporally Resolved Optical Emission Spectroscopy for Investigating rf Plasmas and Micro-Discharges**, ***D. O'Connell***, Queen's University Belfast, Northern Ireland **INVITED**

Non-thermal low temperature plasmas are widely used for technological applications. Increased demands on plasma technology have resulted in the development of various discharge concepts based on different power coupling mechanisms. Despite this, power dissipation mechanisms in these discharges are not yet fully understood. Of particular interest are low pressure radio-frequency (rf) discharges and also more recently developed micro-discharges at elevated pressure. Optical measurements are a powerful diagnostic tool offering high spatial and temporal resolution. Improved advances in technology and modern diagnostics now allow much better temporal resolution and deeper insight into fundamental mechanisms. In low pressure rf discharges insight into the electron dynamics within the rf cycle can yield vital information. The optical emission from these discharges exhibits temporal variations within the rf cycle, requiring high temporal resolution on a nano-second time scale. These variations are particularly strong, in for example capacitively coupled plasmas (CCPs), but also easily observable in inductively coupled plasmas (ICPs), and can be exploited for insight into power dissipation. Interesting kinetic and non-linear coupling effects are revealed in capacitive systems. In the relatively simple case of an asymmetric rf CCP the complexity of the power dissipation is exposed and various mode transitions (gamma-, alpha-mode and wave-particle interactions) can be clearly observed and investigated. Multi-frequency plasmas, provide additional process control for technological applications. Through investigating the excitation dynamics in such discharges the limitations of functional separation is observed. Recently developed micro-plasmas provide reactive plasma environments for processing applications without the need for expensive vacuum systems. On the one hand they allow extremely localised treatment, e.g. localised surgery. On the other hand they can provide the opportunity for controlled and scalable large area treatment using array devices of thousands or millions of micro-plasmas. However, fundamental understanding of the important mechanisms in particular coupling effects between individual discharge devices is to date poorly understood. Time and space resolved optical emission spectroscopy reveal details of these mechanisms.

3:20pm **PS1-ThA5 Time Resolved Studies of Ion Dynamics in an RF-Biased Plasma Reactor**, ***B. Jacobs***, *W. Gekelman,* University of California - Los Angeles, *M. Barnes,* Intevac Corporation, *P. Pribyl*, University of California - Los Angeles

Plasma reactors used in semiconductor processing require precise control over both ion bombardment energy and ion flux to the substrate surface; furthermore these parameters must be uniform over the entire substrate. We report on Laser-Induced Fluorescence (LIF) measurements of the vertical and radial argon ion velocity distributions in a vertical plane above the wafer in an Inductively Coupled Plasma (ICP) Plasma Reactor with a 700 kHz ICP source and a 2 MHz capacitively coupled bias to a 300 mm silicon wafer substrate. The ICP source is capable of pulsed operation with periods of 1 - 100 ms and variable duty cycles. The LIF diagnostic measures ion velocities at over 30,000 points simultaneously in a 10 cm x 8 cm region with a 500 μm spatial and 10 ns temporal resolution. The laser can be phase-locked to either the ICP or capacitive substrate bias source. In this manner, two-dimensional ion distribution functions are investigated as a function of the RF phase of the capacitively coupled substrate bias as well different phases of the ICP pulse period. By combining the LIF data with Langmuir probe and microwave interferometer measurements, we obtain previously unavailable data in relation to the ion dynamics over a 300mm substrate - including ion energy and angular distributions, ion drifts and heat flux, and their spatial variations.

4:00pm **PS1-ThA7 A New Diagnostic Based on Fast Atom-Atom Ionization to Measure the Energy Distribution of a Fast Neutral Beam**, ***A. Ranjan***, *V.M. Donnelly, D.J. Economou*, University of Houston

A new diagnostic was developed to measure the energy distribution of a fast (10s to100s eV) neutral beam. Fast neutrals were allowed to collide with slow (thermal) neutrals in a chamber of controlled background pressure (e.g., 10^{-4} Torr). A fraction of the fast neutrals was ionized as a result of the atom-atom collisions. The ionized species current was measured as a function of energy with a gridded energy analyzer and off-axis channel electron multiplier, housed in a differentially pumped chamber. The energy distribution of the fast neutral beam was determined from the known cross section of the atom-atom ionization collision as a function of energy. The method was applied to measure the energy distribution of a fast neutral beam formed by surface neutralization of ions, extracted through a grid with high aspect ratio holes (neutralization grid). A pulsed-plasma technique was implemented to achieve an ion beam with a tight energy spread. Ion energy was controlled by a DC bias, applied on an electrode in contact with the plasma, during part of the afterglow period. The electron temperature decays rapidly in the afterglow, which yields a nearly uniform space potential, resulting in an ion beam with tight energy spread. The peak of the NED was ~7% lower than that of the parent ion energy distribution (IED), compared to a ~3% expected energy loss, based on specular reflection. The neutral energy distribution (NED) had a larger energy spread as compared to the parent IED. For example, the FWHM of a NED and the corresponding parent IED were 32 eV and 10 eV, respectively. To study the effect of surface roughness of the neutralization grid, results for a metal grid with a "rough" surface (roughness ~ 10s of nm) will be compared with those of a "smooth" (0.15 nm RMS roughness) silicon grid.

4:20pm **PS1-ThA8 Metastable Probe in Remote Helium Plasma**, ***N. Miura***, *J. Hopwood*, Tufts University

An electrostatic probe for measuring helium metastable density was designed and tested in low-pressure, remote helium plasmas. The measured

spatial distribution of helium metastable atoms was then compared with a numerical flow simulation of the plasma. The probe measures secondary electron emission due to helium metastable fluxes at a clean stainless steel surface. The probe consists of a small, planar surface surrounded by an outer guard ring. The outer ring was biased positively to reject plasma ions and the inner part was biased negatively to reject the remaining electrons. In this manner only neutral atoms reach the inner surface, and the inner probe current is due to metastable-induced secondary electrons. Energetic photons generated in the upstream plasma source region were screened from the probe, avoiding photoelectron emission. The experimental gas pressure was 5.5 - 7.5 mTorr inside a 15-cm diameter chamber located downstream from an ICP. Three metastable probes were positioned at different distances downstream from the ICP source and simultaneously swept in the radial direction to obtain spatially-resolved metastable densities. In comparing these measurements to models, the diffusive flow approximation was not completely valid since the mean free path of the metastable atoms was not negligible relative to the chamber dimensions.[1] Therefore, the metastable flow was simulated by both the continuous fluid model and the Monte Carlo method. The results are compared and discussed. The conventional method to measure metastable density is optical absorption, which is well-established and non-invasive.[2,3] That technique gives the density integrated along the optical path and lacks spatial resolution unless Abel inversion is applied. The probe method described here has good spatial resolution, but it is invasive and the secondary electron emission yield is very sensitive to the probe's surface cleanliness.[4] The probe also relies on electrostatic screening due to the biases applied to its surfaces, so the method is only practical in regions of low electron density such as remote plasmas (~10^8 cm^{-3}).

[1] P.J. Chantry, J. Appl. Phys. 62, 1141 (1987).
[2] A.V. Phelps, Phys. Rev. 99, 1307 (1955).
[3] K.E. Greenberg and G.A. Hebner, J. Appl. Phys. 73, 8126 (1993).
[4] T.A. Delchar, D.A. McLennan, and A.M. Landers, J. Chem. Phys. 50, 1779 (1969).

4:40pm **PS1-ThA9 Etch Process Control with a Deposition-Tolerant Planar Electrostatic Probe**, ***J.P. Booth****, D. Keil, C. Thorgrimsson, M. Nagai, J. Kim, L. Albarade*, Lam Research Corporation

We have implemented the deposition-tolerant ion flux probe described by Braithwaite et al.[1] as an in-situ process monitoring sensor on a commercial dielectric etch tool. The probe head is integrated into the upper (grounded) electrode and is made of the same material, and has been shown to have negligible process impact. With the use of an embedded digital signal processor to analyze the current-voltage characteristics in real-time, this sensor delivers high-precision time-resolved measurements (at 10 Hz) of the ion flux, electron temperature and probe floating potential. In addition, if there are thin films deposited on the probe, the film thickness and conductivity can be determined. This gives unprecedented insight into the power delivery, gas composition and surface state of the reactor during wafer processing. This talk will explore how this information can be used to improve the yield, throughput and cost-of-ownership of production etch tools.

[1] N. St.J. Braithwaite, J.P. Booth, and G. Cunge, Plasma Sources, Science and Technol., 5, 677, (1996).

5:00pm **PS1-ThA10 A New Diagnostic Tool of Radio-Frequency Etching Plasma Produced in Insulated Vessels**, ***H. Shindo****, K. Kusaba*, Tokai University, Japan

A new method to measure electron temperature and electron energy distribution function by an emissive probe has been proposed.[1] The method is based on measurement of the functional relationship between the floating potential and the heating voltage of emissive probe. From the measured data of the floating potential change as a function of the heating voltage, the electron temperature could be determined by comparing with the theoretical curve obtained under the assumption of Maxwellian distribution. The overall characteristic of the floating potential change could be explained as a function of the heating voltage. The electron temperatures obtained by the present method were consistent with those measured by the rf-compensated Langmuir probe within the error. These experimental verifications were made in the electron density range of $2.6x10^{11}$–$2.8x10^{12}$ cm^{-3} in an inductively coupled plasma of Ar. In this study, a prototype of the diagnostic tool based on the present method was developed in a computer-aided fashion. The method was also applied to a SF_6 etching plasma which was produced in ceramic discharge tubes by surface-wave with the frequencies of 13.56 and 60 MHz. In this experiment, the Renium filament was employed, and the erectron energy as well as the potentials were measured in SF_6 plasma. These data were found to be consistent with the Si ecth rate obtained in the SF_6 plasma. It was stressed that the present method was advantageous in that the probe is operated in a floating condition, hence applicable to plasmas produced in an insulated container. The electron energy distribution function was also obtained in. SF_6 etching plasma which was produced in ceramic discharge tubes by surface-wave.

[1] K. Kusaba and H. Shindo, Review of Scientific Instruments, 78,123503(2007).

5:20pm **PS1-ThA11 Near-Real-Time Two-Dimensional Wafer Surface Measurements for Process Optimization and Control**, *C.T. Gabriel,* Spansion, Inc., ***G. Roche***, KLA-Tencor

Optimizing and monitoring plasma etching processes has always relied on one-dimensional data provided by the plasma tool (reflected power, Vdc, optical emission intensity, etc.) or by post-etch measurements such as critical dimensions or film thickness changes. It has long been desired to monitor the plasma condition across the wafer surface in real time. Wafer-level sensors have been developed to measure the temperature of the wafer surface in near real time, and now sensors are being developed to monitor other plasma parameters in a similar way. Here we present measurements of Vrf, a parameter related to the plasma potential, taken from a two-dimensional array of sensors across the surface of a 300 mm wafer processed in a multi-frequency, capacitively coupled industrial plasma for dielectric etching. We show the relationship between Vrf and several process parameters, including RF power, pressure, and CO flow rate. The one-dimensional electrostatic chuck voltage, Vesc, does not respond to these parameters in the same way. Some plasma transients were detected by Vrf that were not detected by Vesc or by optical emission intensity. Vrf appears to correlate with plasma density, and because it is an array of detectors, it proved useful in identifying degraded plasma uniformity at lower CO flows. Such wafer-level Vrf measurements may be valuable for applications such as plasma monitoring, chamber matching, and process optimization to minimize plasma process induced damage.

Plasma Science and Technology
Room: 306 - Session PS2-ThA

Plasma Deposition and Plasma Enhanced Atomic Layer Deposition and Etching
Moderator: W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS2-ThA1 High Quality Thin Films Deposited at Low Temperatures by Plasma Enhanced ALD and CVD Techniques**, ***C.J. Hodson****, O. Thomas, Q. Fang*, Oxford Instruments, UK **INVITED**

Low temperature deposition of thin films is becoming increasingly important with a growing range of low thermal budget materials being used in device research. The rapid development and predicted future market for plastic electronics has resulted in a greatly increased focus on thin film depositions below 150ºC. This contribution will address the challenges of low temperature deposition in the context of some example applications including; depositing directly onto photo-resist for lift-off, Si_3N_4 MIM capacitor technology for MMIC and RF-MEMs[1] and Al_2O_3 moisture permeation barriers for polymer based devices such as flexible OLEDs.[2] The study will focus on two chemical vapour deposition (CVD) techniques ideally suited for low temperature deposition namely; Inductively Coupled Plasma CVD and Remote Plasma Atomic Layer Deposition. For any thin film CVD process it is widely true that film quality will degrade at lower temperatures. This degradation is most often measured by decreasing film density, refractive index, breakdown voltage and adhesion; and increasing film impurities and wet etch rates. By using the energetic and reactive plasma species to replace thermal energy it is possible to deposit films with acceptable quality at room temperature, i.e. 25ºC. By generating the plasma remotely such improved film quality can be achieved with low plasma damage to the substrate.

[1]Low temperature high density Si_3N_4 MIM capacitor technology for MMMIC and RF-MEMs applications. K. Elgaid, H. Zhou, C. D. W. Wilkinson and I. G. Thayne, Microelectronic Engineering, Volumes 73-74, June 2004, Pages 452-455

[2]Plasma-assisted atomic layer deposition of Al_2O_3 moisture permeation barriers on polymers. E. Langereis, M. Creatore, S.B.S. Heil, M.C.M. van de Sanden, and W.M.M. Kessels, Appl. Phys. Lett. 89, 081915 (2006).

2:40pm **PS2-ThA3 An Analysis of the Deposition Mechanisms Involved During Self-limiting Growth of Metal Oxides by Pulsed PECVD**, *M.T. Seman,* CMD Research LLC, *D.N. Richards,* ***C.A. Wolden***, Colorado School of Mines

Self-limiting deposition (~ 1 Å/pulse) of several metal oxides (Al_2O_3, TiO_2, ZnO, TiO_2) has been achieved by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process a metal precursor and O_2 are delivered continuously to a PECVD reactor while the rf power is pulsed at low frequency (~ 1 Hz). With proper reactor design and operation the net deposition rate of pulsed PECVD exceeds that of continuous wave operation, and the quantity of impurities is dramatically attenuated. The growth mechanism of alumina from trimethyl aluminum ($Al(CH_3)_3$, TMA) was investigated by comparing the results from pulsed PECVD with those of plasma-enhanced atomic layer deposition (PE-ALD). For both processes

the rate/cycle saturated with ~200 L of TMA exposure. At 165 °C a rate of 1.37 Å/cycle was obtained using PE-ALD. For pulsed PECVD the rate scaled linearly with the TMA partial pressure, and its extrapolation was in good agreement with PE-ALD. The results suggest that deposition in pulsed PECVD involves an ALD component which is supplemented by PECVD growth, and that the contribution of the latter may be tuned using the TMA partial pressure. Experiments using patterned wafers supported this hypothesis. Conformal coatings were observed within 10:1 aspect ratio trenches using pulsed PECVD, however the deposition rate on the surface of these substrates was greater than within the trench. The ratio between the two corresponds well to the ratio of rates obtained from pulsed PECVD and PE-ALD on planar substrates. With cycle times < 1 s, net rates > 30 nm/min were obtained by pulsed PECVD while retaining high quality and digital control.

3:00pm **PS2-ThA4 Self-Limiting Growth of Titania by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***N.G. Kubala***, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of titanium dioxide by pulsed plasma-enhanced chemical vapor deposition (PECVD) at low temperature (< 150ºC). In this process the titanium tetrachloride (TiCl4) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. The as-deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), and dielectric performance. In addition, the plasma chemistry in this system was characterized using quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES). QMS measurements confirmed that TiCl4 and O2 are inert in this system in the absence of plasma. During continuous wave plasma operation TiCl4 is completely consumed, no deposition is observed, and the main byproducts are Cl/Cl2. While no film growth is observed with the plasma on or off, self-limiting deposition was readily obtained by pulsing the plasma at low frequency (~1 Hz). The deposition kinetics and film quality were evaluated as a function of precursor exposure, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TiCl4 concentration and pulse duration, the depositing rate may be adjusted over a narrow range (0.6 – 1.3 Å/pulse). High refractive indices were obtained, scaling with exposure and plasma power over a range of 2.3 to 2.6 at 580 nm. The deposition rate also decreased with plasma power, and OES was used to highlight the role of atomic oxygen in this process. XPS analysis showed that the titanium was fully oxidized. At low plasma power a small amount of Cl contamination was observed, however no Cl was detected in films deposited at higher powers. FTIR characterization of these amorphous films display broad absorption features at low wavenumbers that are distinct from the sharp peaks associated with the crystalline phases of TiO2. A comprehensive analysis of dielectric performance is underway and will be reported at the symposium.

3:20pm **PS2-ThA5 Capillary Jet Injection of SiH_4 in the HDP-PECVD of SiO_2: What We Can Learn from It**, ***R. Botha***, *T. Novikova*, *P. Bulkin*, LPICM, Ecole Polytechnique, France

This paper reports on the deposition of silicon dioxide films from a silane/oxygen gas mixture in a matrix distributed ECR PECVD system. In order to investigate the influence of the primary silane flux and the precursor consumption on the deposition rate and material properties, undiluted silane is first injected into the system through a gas ring positioned around the periphery of the substrate holder, at a distance of 3 cm. The same set of depositions is then done using a 1 mm diameter capillary tube located 3 cm vertically above the substrate surface. The microwave power, pressure, substrate bias and silane gas flow are varied. The material properties are studied using spectroscopic ellipsometry, FTIR spectroscopy and transmission measurements. The plasma is characterized using optical emission spectroscopy (OES) and differentially pumped quadrupole mass spectrometry (QMS). The maximal deposition rate when using a 16 sccm SiH4 and 40 sccm O2 gas mixture is found to increase from 1 nm/s up to 2.16 nm/s when the gas ring is replaced with the capillary jet injection system. This increase is attributed to the large increase in the primary flux of undissociated silane onto the substrate surface. Using an intentionally inhomogeneous deposition resulting from the capillary jet injection and studying the thickness normalized OH absorption in the deposited film at various distances from the capillary injection point, we gain insight into the contribution of the partial pressure of water (which is the main by-product of the reaction between silane and oxygen) on the OH content in the silicon oxide. It is observed that the silicon oxide deposited directly below the capillary injection point has an integrated OH absorption band intensity which is approximately half that of a point 3 cm away from it. Reducing the distance between the injection point and the substrate also leads to a narrowing of the OH absorption band, where the associated vibration mode at 3350 cm-1 practically disappears and only the isolated Si-OH vibration bonds at 3650 cm-1 are retained. By looking at the films thickness at various distances from the capillary jet, it is seen that the primary, beam-like SiH4 is the largest contributor to the deposition rate when using a capillary jet. A Direct Simulation Monte Carlo (DSMC) technique is used to model the flux of the precursor gases onto the substrate plane. The simulation results are compared with the experimental findings.

4:00pm **PS2-ThA7 High Quality TEOS Oxide Film CVD by Microwave RLSA Plasma**, ***H. Ueda***, *Y. Tanaka*, *Y. Ohsawa*, *T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

A high-quality dielectric film CVD in low temperature is required in the processes of nano scale VLSI devices, FPDs, image sensors and flexible organic electronics. There have been many trials to form a high-quality low-temperature silicon dioxide using SiH4-O2 or TEOS-O2 PE-CVD methods. However, they have problems with not only their silicon oxide film qualities but also plasma-induced charging damages to underlying transistors during the plasma process. For example, with regard to the SiH4-O2 PE-CVD, it is hard to exclude Si-H and Si-OH bonds thoroughly to improve electrical properties such as leakage current and dielectric constant. For TEOS-O2 PE-CVD, unreacted TEOS precursor associated with carbon contaminations causes reliability problems and the Si-H and Si-OH contamination was reduced by controlling the plasma source power and Ar gas addition. We report a new low temperature (< 400C) PE-TEOS CVD technology using Microwave (2.45GHz) RLSA (Radial Line Slot Antenna) plasma.[1] It realizes high quality silicon dioxide film without causing charging damages. The film property is as good as a HTO (> 800C) with a good step-coverage performance. The 5%HF wet etch rate of the film is less than that of HTO. One of the unique characteristics of the Microwave RLSA plasma is its plasma generation and transportation system. A very high electron temperature region to produce high density plasma is located just beneath a quartz plate under a microwave antenna. The plasma diffuses to wafer region and the electron temperature in the wafer region becomes less than a half of it in the plasma production region. The electron temperature and density above the wafer in the RLSA plasma chamber can be controlled to produce desired proper precursors for an excellent CVD film by adjusting the pressure, material gas mixture ratio and position of the gas injections. To make the excellent silicon oxide film, the RLSA plasma produces specific precursors with plenty of sufficient oxygen radicals in the gas phase and supplies to the substrate surface. It also seems to provide ions with certain range of energy, that inhibits remaining C=C or C=O bond in the film but enough to proceed surface reaction. In the system, plasma charging damages were never observed even in a MOS capacitor TEG with an antenna-ratio of 1 M, because of the low electron temperature and uniform plasma potential above the wafer surface.

[1]C. Tian, et al.: J. Vac. Sci. Technol. A24 (2006) 1421.

4:20pm **PS2-ThA8 Plasma Polymerization on Textiles: Deposition of Functional Nanostructured Thin Films**, ***S. Guimond***, *Y. Geng*, *A. Ritter*, *B. Hanselmann*, *D. Hegemann*, EMPA, Switzerland

A shift towards highly functional and added-value textiles is now recognized as being essential to the sustainable growth of the textile and clothing industry in developed countries. The demand for tailored surface modifications for water repellence, long-term hydrophilicity, anti-bacterial properties, etc, is therefore increasing. At the same time, the environmental restrictions concerning the waste water produced by conventional textile finishing techniques are getting more and more severe. In this context, plasma processing is seen as an attractive alternative method to add new functionalities to textiles since it is a versatile and eco-friendly (dry) technology. Because plasma processing results in a nano-scaled surface modification, it also has the advantage of preserving the bulk properties as well as the touch of the textiles. In this study, plasma polymer thin films have been deposited on various polyester fabrics of defined structure using $NH_3/C_2H_4/Ar$ low pressure RF glow discharges. The films were first characterized using XPS, FTIR and AFM as a function of the plasma process parameters. For a defined range of energy input and NH_3/C_2H_4 gas flow ratio, the coatings are nanostructured and contain predominantly amine functional groups. Interestingly, these films can thus serve as nanostructured templates for further surface functionalization. For example, they can be used to selectively bind acid dyestuff molecules, allowing a very efficient low temperature and substrate independent dyeing. The amine groups contained in the films were also derivatized with molecules containing OH and CF_3 groups. Due to the nano roughness and the high specific surface area of the films, super-hydrophilic or -hydrophobic properties are obtained. The hydrophilicity of the various coated fabrics was compared by monitoring the spreading of water droplets with infrared thermography. Results show that the textile structure has an important influence on the final properties. This is discussed in terms of capillary effects and accessibility of the textiles structures to the plasma species. Finally, the properties of the coated fabrics remain generally rather stable

during abrasion tests, presumably due to the high crosslinking degree of the films. The scalability of the process investigated in this work has been demonstrated using a pilot-scale continuous web coater.

4:40pm **PS2-ThA9 Stable Super Hydrophobic Nanocoatings on Polymers Prepared by Gas Phase Deposition**, ***M. Puttaswamy***, University of Aarhus, Denmark, *K.B. Haugshoj, L. Christensen,* Danish Technology Institute, Denmark, *P. Kingshott*, University of Aarhus, Denmark

The demand for super hydrophobic and oleophobic coatings in technological applications is continuing to increase particularly on inert materials such as polymers. We utilize the method of molecular vapour deposition (MVD) as a gas phase process for depositing highly uniform and conformal nanocoatings on different laser structured polymer substrates using fluorinated silanes. The challenge with such an approach is optimizing the adhesion and stability of the silane layer, particularly under conditions where moisture is present. One approach we are pursuing is to perform several alternating pre-treatments of the polymer surfaces including O_2 plasma treatment followed by gas phase reaction of the resultant hydroxyl groups with trimethylaluminum ($Al_2(CH_3)_6$). Subsequently the surface is exposed to water vapour. The process of alternating exposures to trimethylaluminum and water, known as atomic layer deposition (ALD), is repeated a number of times, generating an alumina (Al_2O_3) surface highly reactive towards fluorinated silanes, perfluorodecyltrichlorosilane (FDTS) – $CH_3(CF_2)7(CH_2)2SiCl_3$. The chemical surface modification schemes when combined with femtosecond laser structuring results in super hydrophobic/oleophobic with contact angles above 150° (with water). The stable silicon dioxide adhesion layer on the structured surfaces is prepared from silicon tetrachloride and water by a CVD process. The so formed silicon dioxide adhesion layer when subjected to sweat test is found to be stable for almost 14 days at 65°C. The conditions for creating such a stable precursor adhesion layer are dependent on the polymer substrate to be coated. The polymers tested in this study include polyoxymethylene (POM), polyethylene terephthalate (PET), polycarbonate (PC) and polyethylene (PE), and the treatment conditions varied including the effect of plasma treatment, precursor composition, and other operational parameters such as temperature, gas flow and treatment time. So, the precise chemical reactions responsible for forming such a stable super hydrophobic coatings, is best understood using angle dependent XPS, TOF-SIMS and contact angle measurements. Characterization using C_{60} ion source on TOF-SIMS provided us the 'softer' depth profiling with increased ion yields. The results are discussed in terms of the molecular mechanisms of adhesion and polymers tested.

5:00pm **PS2-ThA10 Tunable Properties of Plasma-Polymerized Organosilicones**, ***V. Cech***, Brno University of Technology, Czech Republic

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers – the ability to vary and control the degree of its organic/inorganic character (i.e., the carbon content) by the appropriate choice of fabrication variables. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. The organosilicon plasma polymers are widely recognized for their potential not only in optical and electronic applications, but also in composites and nanocomposites with controlled interphase. Plasma-enhanced chemical vapor deposition (PECVD) was used to prepare thin films of tetravinylsilane in a mixture with oxygen gas employing an RF (13.56 MHz) helical coupling pulsed-plasma system. Plasma polymer films of the thickness from 0.02 to 1 µm were deposited on silicon substrates at different powers (0.1 – 10 W) and oxygen content (0 – 79%) in mixture. When an appropriate on-time and off-time is selected for pulsed plasma, the physical and chemical properties of hydrogenated amorphous carbon-silicon oxide alloy (a-SiOC:H) may be controlled by the effective power. We will demonstrate that the mechanical properties (Young's modulus 9 – 24 GPa, hardness 0.9 – 4.1 GPa), optical properties (refractive index 1.58 – 1.68 (633 nm), extinction coefficient 0.05 – 0.19 (250 nm), band gap 1.9 – 2.9 eV), and wettability (water contact angle 50 – 83 deg, surface free energy 35 – 58 mJ/m^2) of the film may be well tuned in correlation with chemical properties (elemental composition, organic/inorganic character C/Si = 2.5 – 8.6, chemical structure) to prepare tailored materials not only for functional interlayer in polymer composites. The construction of multilayers from individual films of tunable properties will be discussed as well.

5:20pm **PS2-ThA11 Plasma Deposited Films Containing Platinum Nanoclusters as Catalysts for Fuel Cells**, *A. Milella*, ***E. Dilonardo***, *F. Palumbo, R. d'Agostino, F. Fracassi*, Università degli Studi di Bari, Italy

Today, the development of fuel cells is a promising solution to the "energy crisis" and the necessity to provide "clean energy" with virtually zero emission. Fuel cells offer the possibility of abundant energy with negligible emission and high efficiency for converting chemical energy into electricity and heat; however, one of the major disadvantage is their high production cost. Extensive studies are currently addressed to the development of new materials with the aim of improving fuel cell efficiencies and decrease production costs. As far as the catalyst is concerned, nanocomposites films consisting of metal nanoparticles embedded in polymeric matrix are very attractive materials because they allow to decrease the overall amount of Pt while providing high surface area. In literature various approaches have been used to incorporate metal nanoparticles into polymers. In this contribution a one-step plasma deposition process is described to obtain an uniform dispersion of small platinum nanoclusters throughout a thin hydrocarbon matrix. These composite films have been deposited by simultaneous plasma-enhanced chemical vapour deposition (PECVD) of ethylene (C_2H_4) and argon (Ar) gas mixtures and RF sputtering of a platinum target. Characterization of platinum-containing plasma-polymerized ethylene films has been realized using X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra-Red spectroscopy (FT-IR), UV-Vis spectroscopy, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Optical Emission Spectroscopy (OES) has been used to correlate the chemical composition of the plasma with the amount of metal embedded in the deposited film. The electrochemical active area of the samples was determined from ex-situ cyclic voltammetry analyses. A comprehensive study on the effect of different plasma parameters (RF power, deposition time, flow rate of gasses) on the chemical composition and structure of the film will be presented. Results show that the platinum content in the coating can be finely controlled by changing the RF power and the monomer flow rate. In particular TEM images confirm that platinum aggregates in crystalline nanoclusters in distributed uniformly in the material. Furthermore the porosity due to the columnar film growth, together with the nanodispersion of the metal clusters, can be advantageously used for catalytic applications.

Thursday Afternoon Poster Sessions

Plasma Science and Technology
Room: Hall D - Session PS-ThP

Plasma Science Poster Session

PS-ThP1 Time-Modulated Etching in a Dual-Frequency Capacitively Coupled Fluorocarbon Plasma, ***S. Jeong****, D. Sung, K. Kim, A. Ushakov, M. Park, S. Cho, S. Kim, H. Park*, SAMSUNG ELECTRONICS, South Korea

Time-modulated etching process in a dual-frequency capacitively coupled fluorocarbon plasma has been investigated. In the pulsed-mode, etching rate non-uniformity decreased compared to the continuous-mode. The non-uniformity further decreased with lowering duty ratio. In addition, we find that more complex dissociation pattern in time-modulated fluorocarbon plasma than in continuous-wave driven plasma. Difference in the number of negative ions for the two different modes has been observed. We also discuss the relationship between the pulsed-mode process parameters and oxide-to-PR selectivities.

PS-ThP2 In-situ Plasma Diagnostics Study of a Commercial High Power Hollow Cathode Magnetron (HCM) Deposition Tool, ***R. Raju****, L. Meng, H. Shin, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The development of special plasma diagnostic techniques is required to characterize the plasmas used in physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PECVD) commercial tools because of the intense deposition environment, non-standard geometry, and non-standard frequencies. A commercial 200mm INOVA high power (36 kW) HCM deposition tool with computer controlled system was set-up and used as a realistic PVD test bed for designing and testing the new plasma diagnostics techniques. A 3-D scanning RF compensated Langmuir probe was designed, constructed and used to get spatial information of plasma temperature and density in the HCM tool at various input power (0-15 kW), pressure (10-70 mTorr) ranges. Measured electron temperature values are in the range of 1-3 eV and the electron density is between 6×10^{10} to 2×10^{12} cm^{-3}. While operating the tool, deposition of metal on the tungsten probe tip and the insulator probe body was observed. In order to sputter away the deposited material from the tip of the probe a self-cleaning in-situ plasma cup was designed. The plasma cup has a side cleaning station so that RF compensated Langmuir probe can be moved into it, cleaned and return to its original condition without being withdrawn from the system. We observed a considerable variation in electron temperature and density values after the probe was exposed in a 2 kW metal plasma for about 10 minutes. After cleaning the probe tip for about 8 minutes we observed a recovery of electron temperature to the initial value, however the measured electron density was not recovered. Further results revealed the importance of other effects such as probe temperature, temperature of the tool and the probe surface condition. The conductivity of the probe body surface decreases with an increase in deposition time. Hence it is necessary to clean the probe body as well as the probe tip to get more reliable plasma parameter values. A new method to clean the probe body in-situ has been implemented and results will be presented. Further experiments have been conducted to find the deposition rates and ionization fraction of the incident metal atom species employing a quartz crystal microbalance combined with electrostatic filters. A full 3-D scan of parameters is presented.

Acknowledgement: This work was supported by an SRC (Semiconductor Research Corporation) contract with Novellus custom SRC funding.

PS-ThP3 Optical and Electrical Diagnostics of an rf-Capacitively Coupled Plasma, ***H.W. Chang****, C.C. Hsu*, National Taiwan University

Diagnostic studies of a low pressure rf capacitively coupled plasma in mixtures of Ar and O_2 were performed. This home-made plasma system has a cylindrical chamber with upper and lower annular electrodes; the electrode height can be adjusted. A voltage and a current probe were used to monitor the voltage and the current waveforms on the powered electrode with the focus of investigating the significance of the harmonics for plasma diagnostics. The amplitude, phase shift, and up-to-the 6th-harmonics of the voltage and current waveforms were recorded. The optical emission of the plasma was monitored using an optical emission spectrometer. It is found in this work that the 3rd and 4th harmonics become more prominent in Ar-rich conditions and the waveform shows a significant distortion from the 13.56 MHz sinusoid. Upon changing the electrode positions, the current and voltage waveform amplitude as well as the optical emission intensities of multiple peaks show variations below 20%. The 3rd and 4th harmonics in the current waveforms show up-to-50% variations throughout the conditions investigated. This suggests that the harmonic is a more sensitive measure for plasma monitoring. The correlation between operation conditions and diagnostic measurements will be established. The implication of the waveform harmonics to plasma processes will also be discussed.

PS-ThP4 Characterization of Dual Frequency Capacitively-Coupled Oxygen Plasmas by Trace Rare Gases–optical Emission Spectroscopy (TRG-OES), ***Z. Chen****, V.M. Donnelly, D.J. Economou,* University of Houston*, L. Chen, M. Funk, R. Sundararajan*, Tokyo Electron America, Inc.

Oxygen-containing plasmas are widely used for etching of fine features in microelectronics manufacturing. Dual-frequency capacitively-coupled reactors offer some advantages over inductive plasmas. The determination of the neutral species density and electron temperature (T_e) as a function of radio frequency (RF) power(s) and pressure are important in the understanding and optimization of the plasma etching processes in these systems. In this study, trace rare gases–optical emission spectroscopy (TRG–OES) was used to measure T_e, in a dual frequency capacitively-coupled oxygen plasma sustained by a high frequency (60 MHz) "source" upper electrode, and a 13.56 MHz voltage applied to the wafer-supporting lower electrode. TRG-OES is a nonintrusive method for determining plasma electron temperature and, under some conditions, electron energy distributions. The method is based on a comparison of atomic emission intensities from trace amounts of rare gases (a mixture of He, Ne, Ar, Kr, and Xe) added to the plasma, with intensities calculated from a model. In the present experiments, a small amount (5%) of a mixture containing 40% Ne, 20% Ar, 20% Kr and 20% Xe was added to the O_2 feed gas. T_e was measured across the plasma at a height of 5 mm above the lower electrode as a function of pressure (2-200 mTorr) at different applied RF powers. Oxygen atom densities were estimated by O-atom optical emission (844.6 nm), and rare gas actinometry (Ar, 750.4 nm). Results illustrated that T_e in an O_2 plasma with 1000 W upper power and no lower electrode power varies inversely with pressure, from 6.8 eV at 2 mTorr to 3.5 eV at 200 mTorr. As power was increasingly applied to the lower electrode, T_e at low pressure (e.g. 2 mTorr) hardly changed while, at higher pressures, T_e increased to the point that at 500 W lower electrode power, T_e was nearly independent of pressure. Percent dissociations derived from O-atom densities were quite low (<5%), even at the highest upper electrode power.

PS-ThP5 Synthesis of Single-Walled Carbon Nanotubes by Oxygen-Assisted Plasma Enhanced Chemical Vapor Deposition, ***S.W. Huang****, C.H. Hsiao, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with CH_4/H_2 gas mixture as base processing gases. A unique $Ni/Al/SiO_2$ nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. The SWNTs were successfully synthesized at a temperature as low as 600°C. Parametric experiments were conducted to optimize the O_2 fraction in the gas mixture. Experimental results show that a low fraction of Oxygen not only increases the growth rate of SWNTs but also improve the quality of the tubes. The SWNTs are damaged, however, if the fraction of oxygen is too high.

PS-ThP6 Characterization of Platinum Catalyst Supported on Carbon Nanoballs Prepared by Solution Plasma Processing, ***Y. Ichino****, K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Nonequilibrium plasma in aqueous solution, which is solution plasma (SP), is expected as a frontier of plasma nanomaterials processing. The SP processing can realize rapid synthesis at low temperature compared to the conventional methods such as chemical synthesis in solution and plasma processing in gas. We had successfully synthesized Au, Pt and FePt nanoparticles by SP processing. On the other hand, carbon nanoball (CNB) is one of carbon nanomaterial such as carbon nanotube (CNT) and fullerene. The CNB is expected as an electrode material for fuel cells. We already have been successful to synthesis well-defined CNBs. In order to improve the energy-conversion efficiency in fuel cells, Pt nanoparticles must be mounted on CNBs in the high density. In this study, we aim to prepare Pt nanoparticles in the high density supported on CNB (Pt/CNB) by using SP processing and to characterize the properties as the electrode for fuel cells. Carbon nanoball was prepared by thermal CVD process. Ethylene was used

as a raw material. Argon and hydrogen ware used as carrier gases. Solution plasma was generated by a pulsed power supply. Tungsten wire coated with alumina was used as the electrodes. 1.44 mM H_2PtCl_6 solution was added to 50 mg CNB, and polyvinylpyrrolidone (PVP) or sodium dodecyl sulfate (SDS) as a protective agent. After the discharge, the obtained Pt/CNBs were characterized by a scanning transmission electron microscope (STEM), energy dispersive X-ray spectroscopy (EDS) inductively-coupled plasma optical emission spectrometry (ICP-OES). The catalytic properties of Pt/CNB was evaluated by cyclic voltammetry (CV). Color of the solution changed from yellow to dark brown as synthesis time. This change indicates the decrease of H_2PtCl_6 complex in the solution and the improvement of dispersibility of CNB. Moreover, STEM images and elemental mapping images show the Pt nanoparticles supported on CNB. A catalytic activity of the obtained Pt/CNB was shown to be higher than the Pt/CNB prepared by conventional method since the adsorption wave of hydrogen was observed from CV. The activity was varied by the amount of supported Pt nanoparticles, which depended on SP processing conditions.

PS-ThP7 Effect of Dissolved Gases and Ions onto Solution Plasma Fields, ***N. Fujikawa***, *N. Saito, O. Takai*, Nagoya University, Japan

Solution Plasma (SP) is defined as a nonequilibrium discharge phenomenon in liquid solution. The higher reaction rate is expected since it supplies UV light, electrons, and radicals to liquid phase. SP processing is one of attractive reaction field for nano materials synthesis. However, there are few reports on solution plasma processing, in particular, fundamental research. We had been successful to fabricate various nanoparticles such as Au, Pt, FePt, In_2O_3 by SP processing. The reaction mechanism in the solution plasma has not been understood in detail. Reduction must be mainly occurred on these syntheses. However, oxygen and oxygen radical also be produced in the solution plasma. Why does not oxidation proceed? There are many other questions in SP processing. In this study, we aimed to investigate influences of dissolved substance, eg. O_2, ions on the reactive species in the solution plasma. A pulsed power supply was utilized to generate plasma. Needle-shaped tungsten (diameter: 1 mm) was utilized as an electrode. Voltage between electrodes, pulse width and frequency were 2400V, 2μs and 15kHz, respectively. Optical emission spectra were measured with a emission spectrophotometer. Ar or O_2 gases were introduced into the solution in order to vary the amount of dissolved oxygen. Discharge time was 30min. and solution temperature was varied from 10 to 30°C. Moreover, several kinds of chlorides were added into liquid solution in order to observed influences of ions. Peaks attributed to H_α, H_β, H_γ and O were observed in optical emission spectra. The presence originated from decomposition of water. The each intensity is almost constant although the flow rates of O_2 and Ar gases varied. From this, dissolved oxygen did not have a great effect on plasma state. On the other hand, peaks attributed to cation produced from chlorides were observed although peaks of chlorine were not observed. These differences would be discussed from the viewpoint of mobility in the solution, molecular weight, molecular or ion radius, and the reactivity of activated species.

PS-ThP8 Organic Compounds Synthesized by Short-Pulsed Discharge in Aqueous Solution, ***T. Mori***, *K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Some scientists had attempted amino-acid synthesis in order to represent origin of livings. For example, S.L.Miller obtained amino-acid after generating cyanide and aldehyde from discharged mixture gas, which consisted of NH_3, CH_4, H_2 and H_2O. This gas is main composition in primitive atmosphere in ancient times. Recently, we had been successful to generate solution plasma, which is one of pulsed discharge phenomenon in the solution. This is nonequilibrium plasma in solution. Thus, we can form cold plasma in the solution. Solution plasma supply many amount of radicals, ions and electrons, and intensive ultraviolet even at room temperature. Such state might be found on the earth, in particular, near seawater surface. In this study, we attempted to synthesize amino-acid by using the solution plasma in C-H-O-N solution system. As first experiments, organic synthesis with solution plasma was conducted in methanol and water system. Solution plasma was generated by using a short-pulsed power supply. After discharge, the ninhydrin solution was added to the obtained solution in order to confirm the formation of amino-acid through ninhydrin reaction. When amino-acid is produced, the color of the solution changes into Ruhemann's purple. Moreover the product in the solution was analyzed by nuclear magnetic resonance (NMR). While the ratio of methanol to water was varied, the amount of products and their species were investigated in detail. Solution plasma was generated in solution consisting of ethanol and water. Formation of acetaldehyde in the solution was confirmed by silver-mirror reaction and NMR analysis. Formation of CH_4, H_2 and O_2 gases was also confirmed by gas chromatography. The gases might be produced via several recombination reaction between radicals in the solution plasma. Additionally, while the ratio of ethanol to water was varied, the generation amount of CH_4 and H_2 changed drastically. The variation of ratio has a great influence on excited state and the reaction in the solution plasma. The productants synthesized in other solutions were discussed as same manner.

PS-ThP9 Excited Species by Shorter-Pulsed Electrical Discharges in Aqueous Solutions: Effect of Electrodes with Low Work Function, ***C. Miron***, *M.A. Bratescu, N. Saito, O. Takai*, Nagoya University, Japan

Pulsed electrical discharges in water have shown to produce hydrogen, ozone, oxygen, hydroxyl radicals and other chemically active species, making these techniques useful for several applications, such as water purification, nanoparticles synthesis. The electrical discharges in liquids were realized using different types of electrodes, such as copper, tungsten, stainless steel. During the experimental work many difficulties have been encountered due to the sparks and electrodes erosion process. Electrodes of high melting point, corrosion-resistant and high stability are required in realizing the electrical discharges in liquids. The objective of the present work is to investigate the optical properties of a pulsed glow discharge in ultrapure water between two electrodes with low work function, such as lanthanum hexaboride and tungsten. The effect of the electrode material on some physicochemical processes generated in solution plasma was realized by using time-resolved optical spectroscopy technique. Lanthanum hexaboride (LaB6) cathode has high stability and a very low work function (2.5 eV) in high vacuum, which changes when temperature is increased. Also is an excellent electron emitter material due to the oxygen adsorption on the lanthanum sites. The lifetime of these cathodes is 10 – 15 times longer than that of the tungsten cathodes. The behavior of the plasma and some properties of the LaB6 and tungsten electrodes, their effects on the time evolution of the reactive species generated in the electrical discharges in water were investigated in the present work. Time-resolved optical spectroscopy of the reactive species generated in the plasma showed a different evolution in time, depending on the electrode material, the life time of the excited species, and pulse polarity of the applied pulsed voltage. The electron temperature in the plasma was very low when LaB6 electrodes were used in the process, compared to the electron temperature obtained in the atmospheric pressure air plasmas. The low value of the electron temperature explains the broad band spectrum of the molecular species acquired in the electrical discharges generated in ultrapure water.

PS-ThP10 Effects of Vacuum-Ultraviolet Radiation on the Plasma-Induced Charging of Patterned-Dielectric Materials, ***G.S. Upadhyaya***, *J.L. Shohet*, University of Wisconsin-Madison

In this work, the effects of vacuum-ultraviolet (VUV) radiation on plasma-induced charging of patterned-dielectric structures are investigated. Experimental results show that supplemental-VUV radiation exposure of patterned dielectrics is beneficial in minimizing the plasma-induced charge on patterned-dielectric structures. The results of this work indicate that exposure of patterned-dielectric materials to VUV radiation during plasma processing can be useful in reducing or eliminating structural and electrical damage caused to patterned dielectrics by electron shading. Investigation of the effects of VUV radiation on the plasma charging of dielectrics was accomplished by evaluating the response of unpatterned, plasma-charged, oxide-coated samples exposed to monochromatic-synchrotron-VUV radiation at the University of Wisconsin-Synchrotron Radiation Center. VUV exposure of unpatterned SiO2/Si wafers indicated that photon energies less than or equal to 11 eV are beneficial in depleting the plasma-induced charge. The radiation-response experiments were subsequently extended to include patterned-dielectric wafers. Specialized, patterned-test structures with different aspect ratios (depth/width of a pit) were charged in a DC plasma and subsequently exposed to monochromatic-synchrotron-VUV radiation. Surface-potential measurements revealed significant charge depletion for photon energies in the range from 8-11 eV thereby indicating the beneficial effect of VUV radiation during plasma processing of patterned dielectrics. In addition, it was observed that the number of photons required to deplete charge in patterned dielectrics increases with the increasing aspect ratio of the pits in the patterned wafer. The experimental results are explained with equivalent-circuit models which suggest that electron photoinjection from the Si substrate as well as oxide surface conductivity play an important role in depleting the plasma-induced charge on the patterned-dielectric materials. Thus, we conclude that plasma-charging-induced damage in patterned-dielectric materials can be minimized by supplemental VUV exposure of the wafers during plasma processing.

Work supported by NSF under Grant DMR-0306582 and in part by the Semiconductor Research Corporation under Contract 2008-KJ-1781. The UW Synchrotron is a National Facility supported by NSF under Grant DMR-0084402. *G.S. Upadhyaya present address: Lam Research Corp., Fremont CA. .

PS-ThP11 How Far Should Be for Being Remote Plasma?, ***Y. Kim***, *W.K. Yang, J.H. Joo*, Kunsan National University, Korea

Remote plasma has been used in PEALD to reduce adsorbed precursor into a compound layer like HfO_2. The demanding role of plasma is a supplier of radicals not ions which might induce charge damage to devices. We focused the effects of plasma in two aspects; ion transport and thermal energy transfer to the wafer which have been underestimated in previous works. Advanced Energy's Remote Plasma Source is installed 300mm above a wafer and operated at a few to hundreds of mTorr range, within 1.5kW. Plasma was well localized within the quartz chamber region at high pressure regime due to reduced mobility of charged particles. At 10mTorr, plasma was spread to all over the chamber. Measured surface temperatures at four points from the wafer showed 50, 70, 150, and 600°C within a minute from ignition of Ar ICP(~2MHz, 500W). Temperature rise at the wafer surface could be from three mechanisms: ion kinetic energy, ion and meta-stable recombination heat release. We developed a 2D and 3D fluid based model using CFD-ACE+ to investigate heat transfer from plasma source including chamber outside cooling by air.

PS-ThP12 Real Time Feedback Control of Plasma Density by using a Floating Probe in Inductively Coupled Plasmas, ***S.H. Jang***, *M.H. Lee, C.W. Chung*, Hanyang University, Republic of Korea

A real time feedback control of plasma density to apply processing plasmas was carried out experimentally in inductively coupled plasma (ICP). The plasma density control can contribute good processing performance because etched and deposition rate are generally a function of the plasma density, and it influences other processing parameters such as the number of radicals, uniformity, processing time etc. In this study, the plasma density was measured by a floating probe which can measure the plasma density in real time without plasma perturbation installed as a sensor on a chamber wall, and the measured information was fed back to actuator to influence the plasma density. This plasma control system allowed the plasma density to reach and keep the desired densities below 0.1% of the state error. To describe External disturbances, the pressure of the chamber was dropped from 10 mTorr to 5 mTorr by using a molecular flow controller. At the pressure disturbance, the density decreases, and recovers with 1.5% of the maximum error and 10 s of the settling time. In the comparison of active and inactive control with pressure disturbance, the Maximum state errors were 1.5% and 40% respectively.

PS-ThP13 Time Resolved Measurements of the Electron Density with a Cutoff Probe in a Pulsed Plasma, ***J.-H. Kim***, *S.J. You,* Korea Research Institute of Standards and Science*, B.-K. Na,* Korea Advanced Institute of Science and Technology*, D.-J. Seong, Y.-H. Shin*, Korea Research Institute of Standards and Science

In pulse-modulated capacitively coupled plasmas generated in Ar/CF4 mixtures, time variations of the electron density were measured with a cutoff probe. For measuring the cutoff frequency, a microwave is introduced through a radiating antenna to the plasma, and the transmitted wave is detected on a receiving antenna connected to a port of an oscilloscope. From the transmission spectrum we obtained the wave cutoff frequency, which could directly give the electron density. To measure the time variation of cutoff frequency, we scanned the transmitted signal with time for a fixed frequency, which was done for next fixed frequency and so on. Thus, we accumulated the time variations of the transmitted signal data for each different frequency and transposed the data array. Therefore, we obtained the time variation of the cutoff frequency. We investigated the decay time of the electron density for different pressures, repetition frequencies of the pulse modulation, and duty ratios.

Plasma Science and Technology
Room: 304 - Session PS1-FrM

Plasma-Surface Interactions in Materials Processing II
Moderator: T. Kropewnicki, Freescale Semiconductor

8:20am **PS1-FrM1 Effect of Annealing Temperature on the Response of HfO_2 to Vacuum Ultraviolet Radiation**, ***J.L. Shohet***, *J.L. Lauer, G.S. Upadhyaya,* University of Wisconsin-Madison, *Y. Nishi*, Stanford University

The integration of high-k/metal gate stacks into CMOS technology poses several integration problems for the microelectronic industry. The metal gate electrode is often deposited on the high-k dielectric using plasma-sputter deposition; as a result, the high-k dielectric will be directly exposed to the plasma during metal-gate deposition. Plasma-induced charging damage from energetic electrons, ions, and photons has been found to degrade the electrical characteristics and reliability of the gate dielectric. In this work we use synchrotron radiation to determine the role that VUV radiation has in the production of electron-hole pairs created in HFO2 dielectrics on Si wafers with conductivities of 1000 and 4000 Ohm-cm. We determined the general valance band structure of the HfO2 dielectrics in the photon energy range of 5 and 30 eV. Since Argon is the feed gas most often used in plasma sputter deposition we determined the response of HfO2 films with thicknesses between 4 and 20 nm to the Ar-I emission line at 106.6 nm (11.6 eV), which is often the most intense emission line from an Ar plasma. After the dielectrics are irradiated with VUV, we measured the surface potential as a function of position across the irradiated region with a Kelvin probe. By measuring the surface potential for various thicknesses we are able to separately determine the density of surface and interface trapped charge. From the trapped charge densities we estimate the voltage across the dielectric during irradiation with the use of a mathematical model. By combining the current measurements with the estimated voltage across the dielectric we can determine the conductivity of the dielectric layers as a function of photon flux density. In addition, we determine the effect of annealing temperature of HfO_2 dielectrics as a function of total photon dose and compare the results to that of SiO2 films of similar thickness. There appears to be a correlation between the VUV-induced current density and annealing temperature with the total-induced charge measured after VUV irradiation.

Supported by the National Science Foundation under Grant Number DMR-0306582 and the Semiconductor Research Corporation under Contract Number 2008-KJ-1781. The Synchrotron Radiation Center is funded by the National Science Foundation under Grant Number DMR-0537588.
*G.S. Upadhyaya present address: Lam Research Corporation, Fremont, CA.

8:40am **PS1-FrM2 Response of BEOL Dielectrics to VUV Radiation**, ***J.L. Lauer***, *J.L. Shohet,* University of Wisconsin-Madison, *Y. Nishi*, Stanford University

Several integration challenges arise during plasma processing of back-end-of-line (BEOL) dielectrics with the scaling of interconnects from the 65 nm to the 45 nm technology node. This work focuses on the role that vacuum ultraviolet (VUV) radiation has in producing and/or mitigating damage to BEOL dielectrics during plasma processing. Vacuum ultraviolet (VUV) radiation with photons in the energy range of 5 to 30 eV produced by high-density plasmas in plasma-processing systems can cause degradation of electronic devices by producing changes in the optical, mechanical, chemical and electrical properties of dielectrics. In particular, VUV radiation is capable of creating electron-hole pairs within dielectrics. As a consequence of the increased conductivity, the dielectric layer acts as an antenna, being able to collect charges from the plasma which can cause charging damage. To determine how VUV can affect the electrical properties of dielectrics, we utilize synchrotron radiation incident on silicon wafers coated with dielectric layers which, in contrast to plasma exposure, has only photon flux incident on the dielectric surface. Measurements of the charging currents during VUV exposure appearing on dielectrics of various thickness and composition were made. In addition, the total induced charge that remains within the dielectric after VUV exposure was measured with a Kelvin probe. We show the effect VUV has on the induced trapped charge and conductivity of porous SiCOH films with dielectric constants between 2.55 and 3.00 for various film thicknesses. In addition, we compare the valence-band structure between 5 and 30 eV for different etch-stop dielectrics (SiN, SiC, oxygen-doped SiC, and nitrogen-doped SiC) and determine how the accumulation of space charge controls the conductivity of these films. These effects are compared with results obtained with SiO_2 to determine the potential integration challenges that these new dielectrics will pose in the future.

Work supported by the Semiconductor Research Corporation under Contract 2008-KJ-1781 and in part by NSF under grant DMR-0306582. The Synchrotron Radiation Center is funded by NSF under Grant Number DMR-0537588.

9:00am **PS1-FrM3 Mechanism of Plasma Ashing Damages on Porous SiOCH Films**, ***H. Yamamoto***, *K. Takeda, M. Sekine, M. Hori*, Nagoya University, Japan

The construction of integration process employing low dielectric constant (low-k) materials for interlayer dielectric is a key for the development of ULSI devices. Since the low-k films tend to be damaged during plasma processes, the damage free plasma processes are strongly required. Although many researchers have been studying on the plasma damage on the low-k films, there has been little in situ evaluation of plasma damages on the low-k films. The in situ evaluation is crucial for the clarification of damage generation mechanism because properties of damaged low-k films change when the low-k films are exposed to atmosphere. We built up an in situ measuring system to evaluate surface properties of the low-k films during plasma process. We investigated H_2/N_2 ashing plasma damages on porous SiOCH films and the correlation between the amount of damages and densities of radicals in the plasma which make large effects on low-k film properties during plasma process. The surface reaction was measured by using in situ Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) and spectroscopic ellipsometry. Absolute densities of H and N radicals were measured by vacuum ultraviolet absorption spectroscopy. The 100 MHz excited capacitively coupled plasma was used for the ashing process. The thickness of damaged layer was measured at a real time by the in situ spectroscopic ellipsometry and in situ FT-IR RAS during the ashing process. After the porous SiOCH were exposed to H_2/N_2 plasma at various flow rate ratios of $H_2/(H_2+N_2)$ for 60s, the thickness of damaged layer was monotonically increased with the flow rate ratio and reached the maximum of 33nm at that of 100%. H radical densities were increased with the flow rate ratio and had the maximum of $7.5x10^{11}cm^{-3}$ at that of 75 %, and then, decreased to $6.8x10^{11}cm^{-3}$ at that of 100%. N radical densities had the maximum of $9.5x10^{11}cm^{-3}$ at that of 25 %. The thickness of damaged layer agreed well with the H radical density in the region for 25% to 75%. Even though the H radical density decreased, the thickness of damage increased at the flow rate ratio of 100 %. On the basis of these results, we consider that damages on the porous SiOCH are determined by chemical reactions of H radicals which enhance the damage reaction and N radicals which have an effect of inhibition of the damages.

9:20am **PS1-FrM4 Surface Modifications of Ultralow Dielectric Constant Materials Exposed to Plasmas under Sidewall-like Conditions**, ***M.S. Kuo***, *G.S. Oehrlein*, University of Maryland at College Park

Fluorocarbon (FC)/Ar based capacitively coupled plasmas (CCP) are widely used for dielectric etch in back-end-of-line (BEOL) processes. During formation of via/trench structures, highly polymerizing FC radicals deposit on via/trench sidewalls in parallel with ion-assisted etching of the dielectric. Since porous ultralow dielectric constant κ (ULK) dielectrics for 45 nm technologies or below are sensitive to plasma damage, FC thin film deposition on sidewalls is examined for its potential to protect ULK against plasma damage during subsequent process steps, e.g. photoresist ashing. For conditions where a small gap, high-aspect ratio structure in conjunction with blanket ULK films is used to simulate surface chemistry aspects of trench sidewalls we find that a thin (~1-3 nm) FC film deposits on the ULK surface and protects the ULK material against damage from other neutrals species, e.g. fluorine. The dependence of protection efficiency on FC film thickness and FC etching chemistry is discussed. The small gap geometry neglects the effect of scattered ions on ULK sidewalls, which potentially may produce surface modifications of actual ULK via/trench sidewalls. We attempted to address the effect of scattered ions, by examining ULK surface portions additionally bombarded by ions deflected at the edge of the gap structure. Fluorocarbon film deposition rates and composition were studied for these surface regions. The influence of these ULK surface modifications on ULK damage during photoresist mask stripping will be evaluated as a function of gap structure geometry, plasma chemistry and ion energy.

9:40am **PS1-FrM5 Degradation Mechanisms of Structure and k Value of Low-k Film by Plasma Irradiation**, ***J. Chung***, *S. Yasuhara,* Tohoku University, Japan, *K. Tajima, H. Yano, S. Kadomura, M. Yoshimaru, N. Matsunaga,* Semiconductor Technology Academic Research Center, Japan, *S. Samukawa*, Tohoku University, Japan

While the feature size of ultra-large-scale integrated circuits (ULSIs) has been shrinking, conventional Al/SiO_2 interconnects have been substituted by Cu/low-dielectric (low-k) film interconnects to reduce the resistance-capacitance (RC) delay and power consumption of the circuits . Since suitable Cu etching processes are not readily available, damascene

processes have been developed for Cu/low-k interconnects. Plasma processes are extensively used for the etching of low-k films. However, since low-k films, such as porous silica films incorporated with methyl groups (SiOC films), are vulnerable to plasma irradiation, low-k films are severely damaged during plasma etching processes. During such processes, methyl groups are extracted from SiOC films due to ion, radical, and photon irradiation from plasma. As a result, the dielectric constant of SiOC films increases during plasma etching processes. We previously proposed a neutral beam process, in which the effects of photon irradiation from plasma can be eliminated, and using this process, we achieved low-damage etching/ashing of low-k films, which is not possible with the conventional plasma process. We speculated that the elimination of photon irradiation was attributed to the low-damage etching of low-k films. Still, the damage mechanism in low-k films during plasma etching has not been fully clarified. Further experiments are therefore needed to fully understand the degradation mechanism of structure and k value of low-k film and influences of ion, radical, and/or photon irradiation on the structure and k value of low-k film during the plasma etching processes. For these reasons, we precisely investigated the changes of structure (linear Si-O, Cage Si-O, Network Si-O, $Si\text{-}CH_3$/Si-O, $Si\text{-}(CH_3)_1/Si\text{-}(CH_3)_1$,and k value by ions, chemical reactions by radicals and ions, and photon irradiation on SiOC films during Ar, CF_4, O_2 and H_2 plasma irradiation. We found that the damage degree of low-k film depends on its structure components ratio.

10:00am **PS1-FrM6 Study of SiOxFy Passivation Layer Deposited in SiF_4/O_2 ICP Discharge used in Cryogenic Alternated Etching Processes**, ***J. Pereira****, L.E. Pichon, R. Dussart, C.Y. Duluard, E.H. Oubensaid, H. Jiang, P. Lefaucheux,* GREMI, France*, M. Boufnichel,* ST Microelectronics, France*, P. Ranson*, GREMI, France

Silicon dry etching is widely used in microelectronics and microsystems industries in order to elaborate high aspect ratio structures [Micro-ElectroMechanical Systems (MEMS), Micro-OptoElectroMechanical systems (MOEMS) or integrated components]. In order to elaborate such deep structures, industry mainly uses the Bosch process, consisting of an alternation of isotropic etching (SF_6 plasma) and deposition (C_4F_8 polymerizing plasma) steps at ambient temperature. Even if this process can be well controlled, it presents many drawbacks such as sidewall roughness due to scalloping effect, or low etch rate. Thus, a new robust process used to form high aspect ratio structures into silicon bulk, called alternated cryogenic process (STiGer) is investigated.[1] Its principle consists of etching a silicon wafer cooled at cryogenic temperature (T~-80°C) by the alternation of isotropic (SF_6) etching steps and plasma deposition steps in SiF_4/O_2 gas mixture. The deposition step leads to the formation of a SiOxFy passivation layer used to protect the sidewalls and enhanced the anisotropic etching.[2] The formation of this passivation layer is not yet well understood, and its study is crucial for improving the cryogenic process. Moreover, fluorine-doped silicon dioxide films deposited by plasma have gained considerable importance for applications as low dielectric constant layers for reducing the capacitance between metallic lines in silicon based high-speed integrated circuits.[3] In this presentation, SiOxFy thin films deposited in ICP reactor are analysed in order to understand their formation and evaluate the effect of various parameters: SiF_4/O_2 gas mixture, substrate temperature, negative bias voltage or source power. The chemical structure and composition of the passivation layer is particularly studied. Fourier-Transformed InfraRed spectroscopy (FTIR) is used in order to determine the molecular groups constituting the coating and particularly the fluorine incorporation within the SiO_2 network and its consequences. Ellipsometric measurements give us informations on deposition rate and films characteristics such as refractive index, n.

[1] T. Tillocher and al., J. Electrochem. Soc., Volume 155, Issue 3 (2008) pp. D187-D191.
[2] X. Mellhaoui and al., J. Appl. Phys., 98 (2005) 104901.
[3] T. Homma, Mater. Sci. Eng., R Rep. 23 (1998) 243.

10:20am **PS1-FrM7 Anisotropic Fluorocarbon Plasma Etching of Si/SiGe Heterostructures and Induced Sidewall Damage**, ***R. Ding****, M.G. Friesen, L.I. Klein, M.A. Eriksson, A.E. Wendt*, University of Wisconsin-Madison

Plasma etching is a critical tool in the fabrication of Si/SiGe heterostructure quantum devices, but it also presents challenges, including 1) control of etch profiles and 2) damage to etched feature sidewalls that affects device performance. 1) Fluorine-based plasma etching often results in device profiles with undercuts due to preferential etching of SiGe over silicon. A C4F8/N2/Ar etch plasma gas mixture introduced here has been successfully used to achieve straight sidewalls through heterostructure layers by formation of a fluorocarbon inhibitor film on feature sidewalls to prevent undercutting. 2) Chemical and structural changes in the semiconductor at feature sidewalls associated with plasma-surface interactions are considered damage, as they affect band structure and electrical conduction in the active region of the device. Here we report the results of experiments designed to better understand the mechanisms of plasma-induced sidewall damage in modulation-doped Si/SiGe heterostructures containing a two-dimensional electron gas (2DEG). Damage to straight wires was characterized both by the width of the non-conductive “sidewall depletion” region at the device sidewall and by the noise level factor, γ_H/N, determined from spectra of the low frequency noise. Observed increases in sidewall depletion width with increasing etch depth are tentatively attributed to the increase in total number of defects with increased plasma exposure time. Excess negative charge incorporated into the fluorocarbon inhibitor film could be another contributing factor. Other factors considered, including defects at the bottom of etched features as well as leakage current bypassing the wire, appear to contribute minimally. The noise level shows a minimum at an ion bombardment energy of ~100 eV, while the sidewall depletion width is independent of bias voltage, within experimental uncertainty. A proposed explanation of the noise trend involves two competing effects as ion energy increases: the increase in damage caused by each bombarding ion and the reduction in total ion dose due to shorter etch times and reduced ion flux to the sidewalls.

10:40am **PS1-FrM8 Influences of Electrical Characteristics in Carbon Nanotubes by Neutral Beam Irradiation***, **A. Wada**, Y. Sato,* Tohoku University, Japan*, M. Ishida, F. Nihey,* NEC Corporation, Japan*, K. Tohji, S. Samukawa*, Tohoku University, Japan

In an effort to realize carbon nanotube FET (CNT-FET), it is necessary to control electrical characteristics of grown CNTs by using plasma processes. However, the conventional plasma process induces severe damages into CNTs because charged particles and ultraviolet photons generate the defects in the CNTs. As a result, the CNT-FET could not be practically fabricated using conventional plasma processes. Here, we have proposed surface modification of CNTs by using our developed neutral beam to slove the problems and to control defects and electrical characteristics. Neutral beam can almost eliminate irradiation of charged particles and ultraviolet photons to CNTs. In this study, we irradiated Ar and N_2 time-modulated neutral beam (TM-NB) to single-walled carbon nanotubes (SWCNTs). Ultra violet-visible-near infrared (UV-Vis-NIR) spectroscopy was performed to understand the electrical characteristics SWCNTs before and after Ar and N_2 TM-NB irradiation. It was observed that Metal/Semiconductor peak intensity ratio was decreased after beam irradiation. This result means that the ratio of semiconductor nanotubes to metallic nanotubes increased after neutral beam irradiation. It is speculated that TM-NB mainly destroys metallic carbon nanotubes. Additionally, UV-Vis-NIR also confirmed that the band gap of SWCNTs was shifted to lower energy by the neutral beam irradiation. This result means band gap energy of SWCNTs can be controlled by the neutral beam irradiation. Based on these results, TM-NB could realize selective breaking of metallic carbon nanotubes and precise control of band gap in CNTs. As a result, we found that TM-NB could control electrical characteristics in CNT-FET.

11:00am **PS1-FrM9 Surface Modification of PTFE Surfaces with Post-Discharge RF Plasmas Operating at Low and Atmospheric Pressure**, ***N. Vandencasteele****, E. Carbone, F. Reniers*, Universite Libre de Bruxelles, Belgium

PTFE samples were exposed to post-discharges of RF plasma operating at low pressure (5 10-2 torr,pure O2) and at atmospheric pressure (Ar-O2). The plasma phase was characterized using optical emission spectrometry (OES). More specifically, the intensity of the O 777 nm line was chosen as a probe for the chemical reactivity of the plasma. The PTFE surface was characterized using monochromatized XPS, dynamic water contact angle, and atomic force microscopy. Depending on the power and treatment time, the surface energy could be either increased or decreased. At low power and/or treatment time, an increase in surface energy due to the grafting of oxygenated polar species is obtained. At high plasma power, a decrease in surface energy, leading, in some cases, to superhydrophobic surfaces is obtained. No oxygen is detected on such surfaces by XPS, and the superhydrophobic behaviour is attributed to an increase in roughness, as evidenced by AFM. By changing the position of the sample in the low pressure system, we could discriminate the role of the electrons, and the one of atomic oxygen. It is suggested that the increase in roughness is due to a chemical etching of the surface, initiated by high energy electrons, and terminated by the formation of gaseous products, CO and CO2, as detected by OES. A reaction mechanism is proposed. Interestingly, similar behaviours are observed using the low pressure system, and the atmospheric pressure system, in one particular geometry. The comparison between low pressure and high pressure results, on the same kind of sample, with the same type of plasma generation (RF mode) opens new routes for the understanding of surface reaction mechanisms at the atmospheric plasma – polymer interface.

This research is funded by the IAP "plasma surface interactions", from the Belgian Federal Government.

11:20am **PS1-FrM10 CoSi$_x$ Damage in Etching and Ashing Plasma**, ***K. Katahira***, Sony Semiconductor Kyushu Corporation, Japan, *T. Tatsumi, S. Kobayashi, M. Fukasawa,* Sony Corp., Japan, *T. Takizawa, M. Isobe, S. Hamaguchi,* Osaka University, Japan, *K. Nagahata*, Sony Corp., Japan

Silicidation of the source/drain is required to produce high-speed CMOS devices, and suppressing the fluctuation of the contact resistance is one of the most important issues. In this study, we clarified the mechanism of fluctuation in contact resistance caused by plasma processes, and we vastly improved the controllability. The relationship between the plasma parameters and the contact resistance to CoSi$_x$ was investigated using a dual-frequency (27/2 MHz) CCP system. A SiO_2/SiN/CoSi$_x$ stacked sample with hole patterns was used. A CF_4 or CH_3F based plasma was used for SiN etching and O_2 or H_2/N_2 plasma was used for the subsequent ashing process. The thickness and composition of the damaged layer were analyzed using XPS, SIMS, and TEM. The ion energy distribution function and the ion penetration depth were calculated using a Monte-Carlo simulation, and a newly developed molecular dynamics (MD) simulation for a Si-O-C-F-H system, respectively. The resistance of the contact increased more when CH_3F was used than when CF_4 used, and a further increase was observed in a high V_{dc} condition in CH_3F. We found that the resistance increase was caused by incident ions from the plasma. The mass number of dominant ions (CH_2F^+; m/e=33) in CH_3F plasma was much lower than that (CF_3^+; m/e=69) in CF_4 plasma. An MD simulation revealed that the dissociated C, H, and F species from CH_2F penetrate deeper than those from CF_3 due to the mass number difference of parent ions. Deeper damage caused by the ion penetration stimulates a deeper oxidation of CoSi$_x$ and raises the contact resistance. We also investigated the effect of the ashing process on the contact resistance. When using a high V_{dc} condition during ashing, the contact resistance increased significantly. In particular, even in H_2/N_2 ashing, not using O_2, the contact resistance increased. When H_2/N_2 plasma, the damage of CoSi$_x$ was formed by deep H penetration. The damaged CoSi$_x$ layer can be readily oxidized during air exposure, resulting in the resistance increase. We observed that the contact resistance has a linear relationship with oxygen concentration in CoSi$_x$. Thus, precise control of the ion energy as well as proper selection of the ion species in the plasma process is indispensable in the fabricating next-generation devices.

Plasma Science and Technology
Room: 306 - Session PS2-FrM

Plasma Processing for 3-D Integration, Photonics, Optoelectronics, and Memory Devices
Moderator: C.C. Hsu, National Taiwan University

8:20am **PS2-FrM1 Silicon Oxide Sidewall Passivation during HBr Inductively Coupled Plasma (ICP) Etching of InP and GaAs Materials for the Fabrication of Photonic Devices**, ***S. Bouchoule***, *S. Guilet, L. Gatilova, G. Patriarche, L. Largeau,* LPN, CNRS, France, *P. Chabert*, LPTP, CNRS - Ecole Polytechnique, France

The ICP etching technique is now widely used for the anisotropic etching of III-V heterostructures, a key building-block for photonic devices. Chlorinated atmospheres are generally used for both InP and GaAs materials, with few studies devoted to HBr. In any case, very few studies exist on the understanding of the sidewall passivation mechanisms occurring during the etching of III-Vs. Using EDX-TEM ex-situ analysis, we have shown for the Cl2-H2 chemistry [JVSTB 26, 666 (2008)] that a silicon oxide layer acting as a lateral etch-inhibitor can build-up on the etched sidewalls of InP-based heterostructures, when a Si wafer is used as the sample tray. This configuration corresponds to most commercial ICP etch systems having an electrode diameter of 4-in or more, used to etch III-V samples of 2-in or less size. In this work, we have analyzed by ex-situ EDX-TEM the passivation layer deposited on the sidewalls of InP and GaAs pillars etched with HBr using a Si tray. A Si-rich layer can build-up on the etched sidewalls under low pressure and high ICP power conditions, leading to anisotropic profiles. The passivation mechanism resembles that identified in Si gate etching using Cl2-HBr-O2 plasmas, and we suggest that a minimum amount of oxygen should exist in the plasma for the passivation layer to build-up. OES measurements indeed showed that oxygen is present in the gas phase, even w/o intentional O2 addition. In our conditions (0.5 mT–1 mT pressure range and ~1000 W ICP power), high values of plasma potential (> 20V) and positive ion current (> 3 mA/cm2) are measured, and oxygen could come from the sputtering of either the Al2O3 ceramic inner parts or the passivated walls of the reactor. We identified that the walls state greatly influences the sidewall passivation process, indicating that the species desorbed from the conditioned walls play an important role. Moreover, we show that adding less than 10 % of O2 to the gas mixture can modify the passivation mechanism: it is strongly enhanced in the case of GaAs material, and the layer is changed from a Si-rich layer to a more stoechiometric SiO2 in any case. The InP and GaAs planar etch rate is also increased, to the benefit of selectivity against dielectric mask, indicating that the concentration of reactive radicals is modified by the addition of a small amount of O2 in HBr. Low loss laser ridge waveguides on InP(311)B substrate and AlGaAs/GaAs microcavities are demonstrated with the optimized process.

8:40am **PS2-FrM2 Low Bias Inductively Coupled Plasma Etching of CdHgTe in CH_4/H_2 Based Chemistry**, ***F. Boulard***, *C. Cardinaud,* IMN CNRS France, *J. Baylet*, LETI-CEA, MINATEC France

CH_4/H_2 based dry etch chemistry is still under study for patterning of high aspect ratio trenches or holes in II-VI compound semiconductor cadmium mercury telluride ($Cd_xHg_{1-x}Te$) used for high performance infrared detectors.[1] Since energetic ions bombardment induces electrical damages,[2] development of a gentle, low bias and chemistry assisted process is investigated. Plasma diagnostics and materials characterizations are developed to obtain a better description of etching fundamental mechanism. Inductively Coupled Plasma (ICP) reactor, allowing decoupling of plasma generation and substrate polarization, is used. Process parameters under study include gas mixture (using CH_4, H_2, N_2 and Ar), bias voltage, source power and substrate holder temperature. Experiments are carried out on alloys which composition varies from x=0.23 to 1. Langmuir probe and mass spectrometry measurements are used to correlate plasma modification induced by N_2 addition to the gas mixture with etched surface characteristics and etch rate. Etch product identification confirms the formation of TeH_2, while direct evidence of $Cd(CH_3)_2$, as proposed in the literature[3,4] is discussed. Post etch quasi in-situ X-ray photoelectron spectroscopy and spectroscopic ellipsometry suggest that etching occurs through a carbonaceous, Cd-rich and Hg-depleted layer. When the bias is significantly decreased to a value as low as 10V and the substrate holder temperature is raised, an average etch rate increase and a strong reduction of the extreme surface Cd/Hg ratio are observed, confirming an enhancement of chemically assisted elimination of Cd. The process developed offers smooth, mirror like, surface morphology and etch rate higher than 300nm.mn^{-1} on $Cd_{0.23}Hg_{0.77}Te$.

[1]A. Rogalski, Infrared Physics and Technology, 50 (2007) 240-52

[2]E. Elkind, J. Vac. Sci. Technol., A 10 (4), (1992), 1106-12

[3]R.C. Keller, M. Seelman-Eggebert, H.J. Richter; J. of Elec. Mat, 24 (9), (1995), 1155-1160

[4]C.R. Eddy, D. Leonhardt, V.A. Shamamian, J.R. Meyer, C.A. Hoffman, and J.E Butler, J. Elec. Mat., 28 (4), (1999), 347-54.

9:00am **PS2-FrM3 Characterisation of InP Ridge Sidewalls Patterned in Inductively Coupled Halogen Plasmas**, ***C. Cardinaud,*** IMN-CNRS, France, *S. Bouchoule*, LPN-CNRS, France

High-aspect-ratio etching of InP-based heterostructures is a critical building block for photonic device fabrication. Indeed highly anisotropic profiles and smooth sidewalls free from undercuts or notches are required to minimize optical scattering losses. Recently it was shown that anisotropic etching can be obtained in Cl2-H2 and HBr inductively coupled plasmas (ICP), due to the passivation of the InP sidewalls by a Si-containing layer originating from the Si sample tray [JVSTB 26(2008)666]. This study is focused on the chemical characterisation by means of X-ray photoelectron spectroscopy of the bottom and sidewall surfaces of InP ridge patterns etched with Cl2-H2 and HBr chemistries. Anisotropic profiles are obtained for low pressure (<1mT), high ICP power (up to 1000W for HBr), H2 percentage (H2%) in the 35-45% range for the Cl2-H2 mixture, moderate dc bias (-140V), sample temperature of ~190°C. ICP etching results are compared to HCl wet etching, taken as reference. Surface chemistry at the pattern bottom can be summarized as follows. Etching in Cl2-H2 with a H2% ~36% gives a surface very close to HCl. Width of the P2p, In3d and In4d InP-bulk contributions are very close to the reference, this indicates that no other species than the oxide is present above the bulk material. The intensity ratios for In/P-bulk (0.9) In/P-oxide (0.6) point out that Cl2-H2 etching produces a slightly P-rich surface. In the case of HBr, the much larger width of the InP-bulk components suggests the occurrence of an additional species that could be amorphous InP. Moreover, an extra component is observed on the P2p spectrum at +0.8eV from that of InP-bulk. In the absence of Br from the surface, we suggest attribution to P-H species. Finally, the high In/P-bulk and In/P-oxide ratios, 4.3 and 3.9 respectively, clearly state that HBr produces an In-rich surface. Sidewall chemistry shows significant differences as compared to the bottom. For example in the case of Cl2-H2, the P2p, In3d and In4d InP-bulk contributions are about 1.5 times larger. Moreover the In/P ratio falls down to 0.4 and about 0.1 for In/P-bulk and In/P-oxide respectively. Opposite, the HCl etched sidewall is identical to the bottom (In/P-bulk = 0.9). For Cl2-H2 etching, this definitely points out a variation of composition in the top 10nm, with a decreasing In/P ratio from the "bulk" to the sidewall surface. Similar analysis are presently carried out on HBr and HBr-O2 etched samples.

9:20am **PS2-FrM4 The Plasma Polymerization of Novel Metal Containing Monomers Via Sublimation of the Precursor Materials**, ***J.O. Enlow***, UES, Inc., *H. Jiang,* Materials Sci. and Tech Applications, LLC, *J.T. Grant,* University of Dayton, *K.G. Eyink,* Air Force Research Laboratory, *W. Su,* AT&T Government Solutions, *A.M. Urbas, T.J. Bunning*, Air Force Research Laboratory

A flowing afterglow plasma reactor has been recently modified to incorporate a custom designed sublimation system for the fabrication of thin films from solid organic monomers. Some metal containing precursors such as ferrocene, as well as Cu, Fe, Mg, Ni, Pb and Zn phthalocyanines and porphorines have been successfully deposited. The optical properties of the films were investigated using variable angle spectroscopic ellipsometry and UV-Vis spectrometry, the chemical composition was determined using FT-IR and XPS and the morphology was examined using AFM and X-ray reflectivity. It was found that due to the incorporation of metal components, these films have relatively high indices of refraction when compared to conventional PECVD hydro-carbon films. Also, through the optimization of the deposition conditions original structural features were maintained in these highly crosslinked thin films. This study demonstrates that the use of sublimation opens up the PECVD technique to a wealth of new solid state and metal containing materials for the fabrication of novel optical and electronic thin films.

9:40am **PS2-FrM5 Advancement and Characterization of 3D TSV Etch Applications**, ***C. Rusu***, Lam Research **INVITED**

Implementation of TSV modules in production for 3DIC applications has become a technical and fundamental reality to contend with. Almost every semiconductor manufacturer is either directly working on TSV module design and development, or – if fabless, is working with partners for implementation of TSV modules. It is clear that CMOS Image Sensors (CIS) are leading the pack in implementation, with memory suppliers following closely. However, it is unclear at this time which memory segment will choose to implement TSV's first; DRAM or Flash, perhaps for reasons more related to economics than technology. This talk will primarily focus on the etch requirements for the TSV module. Etch challenges can vary widely with different applications, such as CIS, Memory, or Logic. In addition, TSV etch challenges vary for different integration schemes, such as via first, via middle, or via last. Therefore, it is without surprise that the TSV etch development tasks have been quite challenging, and existing etch equipment were not immediately applicable for TSV implementation. Recent development and upgrades have been made to address these market requirements, whether for silicon or glass substrates. We will show results of a flexible process system that can etch the multi-film stacks in addition to the deep silicon required to form TSVs. Substrates are patterned with either photoresist or dielectric hard mask, ranging from the micron-level minimum geometries to several tens of microns. TSV etch examples will be demonstrated addressing different integration requirements ranging from patterned photoresist directly on silicon, to patterned photoresist on multi-stack films replicating some of the layers that may exist on processed IC wafers.

10:20am **PS2-FrM7 Investigation of Bottom Profile Degradation Mechanism in Extremely High-Aspect-Ratio Feature Etching**, ***N. Negishi***, *M. Miyake, K. Yokogawa,* Hitachi, Ltd., Japan, *M. Oyama, T. Kanekiyo,* Hitachi High-Technologies Corporation, Japan, *M. Izawa*, Hitachi, Ltd., Japan

As the half-pitch of DRAM design rule advances beyond the 50 nm, precistion plasma etching will be required to realize extremely high aspect ratio feature of over 30. According to the shrinkage of pattern CD and narrowing pattern pitch size, many kinds of profile degradations that occur especially at around bottom area, such as, bottom distortion, twisting, shortage of bottom CD, have been observed. We assume that the mechanism of these etching profile degradations has closely connection with the combination of mask profile deformation, charge-up phenomenon, and the change of etch-front condition at bottom region. In order to diminish these profile degradations, we investigated the mechanism in terms of mask profile deformation effect with using ultra-high-frequency ECR (UHF-ECR) plasma etching system.[1] In this study, we used trench pattern to evaluate the degree of pattern deformation quantitatively as a function of pattern depth. Also, direct observation of etched pattern sidewall with using atomic-force-microscopy (AFM) was applied to clarify the relationship between bottom distortion and mask (necking) profile. The ratio of line width roughness (LWR) to line edge roughness (LER) that estimated from top view observation of etched sample after etch-back process decreased with increasing pattern depth and it means that pattern deformation becomes to 'wiggling' mode at deeper area. On the other hand, AFM observation of etched sidewall revealed that mask (necking) roughness is transferred to the bottom region and amplified drastically. As a result, we confirmed that using the mask of low degree of deformation is effective to diminish the bottom distortion.

(1) K. Yokogawa, N. Negishi, S. Yamamoto, K. Suzuki, and S. Tachi, 1997 Dry Process Symp., pp. 379-383.

10:40am **PS2-FrM8 Very Uniform and High Rate Si Etching Process in Advanced NLD Plasma**, ***Y. Morikawa***, *T. Murayama, K. Suu*, ULVAC, Inc., Japan

High-density of thru silicon via (TSV) is indispensable to the utilization and improvement in performance in 3D-LSI. Advanced high aspect ratio (A/R) TSV etching technologies are required for high-density TSV formation. We have developed a new etching system for TSV and MEMS application. This System provides combined plasma of magnetic neutral loop discharge (NLD) plasma and a sputtering system, which is named as NLD-Si.[1] For high rate silicone etching, it is very important to understand not only high density of the plasma generation but relation between fluorine diffusion (Z: distance of a wafer stage and NLD plasma) and the etching characteristic. In this study, a novel RF antenna 'multi slit rf antenna' has developed for the purpose of high rate etching. The number of slits of the antenna was increased from single line to three parallel lines to extend inductive coupling discharge region. Therefore, high-density generation of both of ion radicals is possible. Each slit interval is 25 cm. And, it is the feature that inductance (L) of this antenna is 0.52 uH and it is low L antenna. As a result of performing electron density measurement of the NLD plasma using this MS-RF Antenna, it succeeded in the high-density plasma production of $1x10^{12}$ / cm^3 by the process pressure of 2 Pa. Next, Si etching process development was performed using the Advanced NLD-Si etcher, which introduced a wafer stage elevator system. Si etching characteristics employing advanced NLD plasma were studied with respect to distance from an antenna. As a result, improvement in the etching rate of 2.5 times or more was realized as a result of optimization of the distance from NL. And, when process pressure and flow rate conditions were made to optimize, about 5 times the etch rate UP was achieved. Finally, the pattern of line width 1um attained the anisotropic etching of 8.5 um/min using Advanced NLD-Si etcher.

[1] Y. Morikawa, et al.; Thin Solid Films 515 (2007) 4918.

11:00am **PS2-FrM9 Fabrication of Very High Aspect Ratio Vertical Through Silicon Via by a Novel Multi-step Plasma Etching Technique**, ***P. Dixit***, Nanyang Technological University, Singapore, *R. Chatterjee,* Georgia Institute of Technology, *J. Miao,* Nanyang Technological University, Singapore, *R. Tummala*, Georgia Institute of Technology

In this paper, we present a novel multi-step etching technique to encounter the aspect ratio dependent etching (ARDE) characteristic of plasma etching process and to fabricate very high aspect ratio vertical through silicon vias. ARDE effect, which represents the reduction in etch rate at higher etching depth, is caused by the the depletion of etching radicals. The collisions of etching species with the outgoing reactions products and with the sidewalls, are also responsible for reduction in the etch rate. To maintain the constant etch rate and vertical sidewall profile, the depletion in the etching radicals should be compensated, which can be achieved by adding more etching radicals and plasma energy. To achieve this objective, we have proposed a multi-step etching technique, in which important DRIE parameters were gradually increased to maintain the constant etching flux . DRIE parameters, such as platen/coil power, SF6 and C4F8 flow rate, etching and passivation cycle duration, etc were increased in steps to provide 'additional etching species' needed at the bottom of the high aspect ratio etched features. At first, effect of individual parameters was investigated by varying a single parameter while keeping remaining parameters constant. 6 DRIE experiments were carried out to evaluate the effect of platen power on the etched profile (8, 10, 12, 14, 16 and 18 W). Similarly other experiments were performed to find the best parameter to overcome the depletion of etching radicals and to maintain the vertical etch profile. When the effect of individual parameters on etched profile was known, those parameters were chosen that gives the straight profile at relatively higher etch rate and with minimum undercut. Effect of platen power on controlling the perpendicularity of through-vias was found to be the most dominant among all parameters. A 200 nm aluminum layer was used as an anti-notching layer to prevent the lateral etching of vias at the bonding interface. Scanning electron microscope confirmed that the etching profile was completely vertical even at an etching depth as large as 510 micron. Using this technique, very high aspect ratio (>30), vertical through silicon vias having an opening dimension as small as 10 micron were fabricated. These DRIE etched through silicon vias were later electroplated to form copper interconnects, which are the most important building blocks for the next generation 3D stacking technology.

11:20am **PS2-FrM10 Through Silicon Via Etching for 3-D Interconnection using Pulse Inductively Coupled Plasma**, ***S.H. Lee**, Y.D. Lim, W.J. Yoo,* Sungkyunkwan University, Korea*, O. Jung, S.C. Kim, H.C. Lee*, Dongbuhitek, Korea

Deep Silicon via etching technology is considered to be a critical and important factor to connect three-dimensional (3D) integrated-circuit system. In this process, the formation of deep Si via etching profiles is an important factor to accomplish filling of the highly conductive metal-materials and operating device in package level. We studied a non-Bosch type deep etching method using the pulse inductively coupled plasma (ICP) for the purpose of improving high aspect-ratio etching profile and reducing undercut at the entrance of the Si vias. We used an ICP etcher (ICP) in which wafer electrode is equipped with pulsing RF bias power which enabled the control of frequency, duty cycle and thereby was expected to affect ion acceleration onto the wafer surface and sidewall passivation of SiOxFy. SF6, O2, and Ar were used to accomplish deep non-Bosch –type Si etching for the pulse plasma discharge. To understand the effects of radicals in the plasma on the formation of etching profiles of deep Si vias, we monitored optical emission of radicals at 419.6 nm for Ar, 703.6 nm for F, and 777.0nm for O.

Advanced Surface Engineering
Room: 204 - Session SE+PS-FrM

Pulsed Plasmas in Surface Engineering
Moderator: A. Erdemir, Argonne National Laboratory

8:20am **SE+PS-FrM1 On the Plasma Parameters in the High Power Impulse Magnetron Sputtering Discharge (HiPIMS)**, ***J.T. Gudmundsson***, University of Iceland **INVITED**

The development of ionized physical vapor deposition (IPVD) was mainly driven by the formation of metal and nitride thin films into deep, narrow trenches and vias that are essential in modern microelectronics. More recently, the control of the ion energy and direction of the deposition species has proved to be an important physical tool in the growth process of new materials and new structures. Over the past few years, various ionized sputtering techniques have appeared that show a high degree of ionization of the sputtered atoms, in the range 50 - 90 %. This is often achieved by the application of a secondary discharge to a magnetron sputtering discharge, either inductively coupled plasma source (ICP-MS) or a microwave amplified magnetron sputtering[1]. High power impulse magnetron sputtering (HiPIMS) is a more recent sputtering technique that utilizes ionized physical vapor deposition (IPVD)[1,2]. High density plasma is created by applying a high power pulse to a planar magnetron discharge. Measurements of the temporal and spatial behavior of the plasma parameters indicate peak electron density of the order of 10^{19} m^{-3}, that expands from the target with a fixed velocity that depends on the gas pressure[3]. The high electron density results in a high degree of ionization of the deposition material. Fractional ionization of the sputtered material has been measured to be over 90 %[2]. The ions are controllable with respect to energy and direction as they arrive to the growth surface. The spatial and temporal variation of the plasma parameters, electron density, electron energy, plasma potential and ion energy, in a HiPIMS discharge are reviewed. The plasma physics of the HiPIMS will be discussed as well as some of applications of the HiPIMS technique.

[1]U. Helmersson, M. Latteman, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson, Ionized Physical Vapor Deposition (IPVD): A Review of Technology and Applications, Thin Solid Films 513 (2006) 1-24

[2]U. Helmersson, M. Lattemann, J. Alami, J. Bohlmark, A.P. Ehiasarian, and J.T. Gudmundsson, Proceedings of the 48th Annual Technical Conference of the Society of Vacuum Coaters, April 23-28, 2005, Denver, CO, USA, p.458

[3] J.T. Gudmundsson, J. Alami, and U. Helmersson, Spatial and temporal behavior of the plasma parameters in a pulsed magnetron discharge, Surf. Coat. Technol. 161 (2002) 249 .

9:00am **SE+PS-FrM3 Deposition of Metal Oxide Coatings using Reactive High Power Impulse Magnetron Sputtering**, ***E. Wallin**, M. Aiempanakit,* Linköping University, Sweden*, T.I. Selinder, E. Coronel,* Sandvik Tooling, Sweden*, U. Helmersson*, Linköping University, Sweden

Metal oxides have been deposited using reactive high power impulse magnetron sputtering (HiPIMS) of metal targets in Ar/O_2 gas mixtures. The use of HiPIMS has in previous studies of deposition of alumina been shown to drastically influence the process characteristics compared to conventional reactive sputtering [Wallin and Helmersson, Thin Solid Films, in press]. Under suitable conditions, oxide formation on the target was found to be suppressed, and the hysteresis effect commonly observed as the gas flow is varied during conventional sputtering was reduced, or even completely eliminated, using HiPIMS. In the present work, these investigations are extended to a wider range of process parameters as well as to other material systems, including CeO_2, in order to better understand the reactive process. Based on this, reasons for the altered process characteristics will be discussed. Moreover, film properties of alumina deposited by this type of process have been investigated. α-alumina was found to form readily on both cemented carbide and Mo substrates at a temperature as low as 650 °C. α phase growth was retained over the studied range of substrate bias voltages (from floating potential to -100 V), while growth at lower temperatures resulted in the formation of γ-alumina at 575 °C and x-ray amorphous films at 500 °C or lower. The film microstructure was studied using electron microscopy techniques, revealing a plate-like structure of the α-alumina films with wider grains and a denser structure for higher bias values. Reasons for the phase composition and microstructure observed with different process parameters will be discussed together with possible pathways for further reduction of the α-alumina growth temperature and improvements of the microstructure.

9:20am **SE+PS-FrM4 A Mass/Energy Analysis of the Plasma during Modulated Pulse Power Sputtering**, ***W.D. Sproul***, Reactive Sputtering, Inc.*, J. Lin, J.J. Moore, M. Hasheminiasari,* Colorado School of Mines*, R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

During modulated pulse power (MPP) sputtering, there are multiple steps within the overall pulse. Usually there are 3 steps, but there can be many more if needed. The first step is the application of a high voltage to the cathode that ignites a weakly ionized sputtering plasma. This weakly ionized plasma is allowed to stabilize in step 2, and then the voltage to the cathode is increase to transition the plasma into a strongly ionized plasma in step 3. This strongly ionized plasma is characterized by a significant increase in the current to the cathode accompanied with a moderate voltage increase. The overall power to the cathode is thus also greatly increased. At the substrate when a bias is used, there is also an increase in the substrate ion current density during step 3, and this ion current density increases as a function of the peak power. The deposition rate for the Cr films is a function of the peak power on the target, but there is a pronounced increase in the deposition rate when the peak power exceeds approximately 100 kW. In this study, a mass/energy analyzer was used to characterize the species in the plasma during the different steps of MPP sputtering of Cr films. Cr plus one ions were readily detected by the mass/energy analyzer in step 3 of the pulse, but it was more difficult to detect multiply charged Cr ions due to the location of the analyzer with respect to plasma and the target. It is possible that multiply ionized Cr ions are not detected due to charge exchange collisions in the plasma. The changes in the species in the plasma will be correlated with observed changes in the structure and properties of the Cr films deposited under different peak power conditions.

9:40am **SE+PS-FrM5 Process, Structure and Properties of Chromium and Chromium Nitride Coatings Synthesized using Modulated Pulse Power (MPP) Sputtering**, *J. Lin, Z. Wu,* Colorado School of Mines*, W.D. Sproul,* Reactive Sputtering, Inc.*, B. Mishra, **J.J. Moore**, M. Hasheminiasari,* Colorado School of Mines*, R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue and achieves the enhanced plasma ionization through modulation of the pulse shape, intensity, and duration. In the current studies, Cr and CrN coatings were synthesized using MPP under different pulse durations and different combinations of the voltage rise and fall times, which were found to exhibit strong influence on the deposition parameters. It was found that the target power, voltage, current, and ion current density were increased with an increase in the long pulse durations and the voltage rise time. For Cr coating depositions, the MPP exhibits higher deposition rates than in the dc conditions when the average power is above 10-12 W/cm^2. A high deposition rate of 230 nm/min for the Cr coating deposition can be achieved with optimized pulsing parameters. The structure of the Cr and CrN coatings were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanical and tribological properties were measured by performing depth-sensing nanoindentation tests, micro-scratch tests and a ball-on-disc wear test in ambient atmosphere. It was found that the microstructure of the coatings changed from large columnar grains to dense and fine nano grains with an increase in the power and ion current densities on the target. A high hardness of 18 GPa has been achieved in Cr coatings deposited with an average power density of 21 W/cm^2 and an ion current density of 1.2 A/cm^2 on the target with a floating substrate bias.

10:00am **SE+PS-FrM6 Deposition Rate of High-Power-Pulse Magnetron Sputtering Processes**, ***J. Emmerlich**, S. Mráz, S. Konstantinidis,* RWTH Aachen University, Germany*, R. Snyders,* University of Mons, Belgium*, J.M. Schneider*, RWTH Aachen University, Germany **INVITED**

In high power pulsed magnetron sputtering (HPPMS), a large power density is applied giving rise to a high degree of ionization. From an application point of view, the major drawback of this technology is the considerably lower metal deposition rate as compared to DC magnetron sputtering. Using transport-of-ions-in-matter simulations (TRIM), it is shown that the apparently low deposition rate can be understood based on the non-linear energy dependence of the sputtering yields. The simulations are consistent with deposition-rate measurements on Cu films as well as with published deposition rate data for Ti [Konstantinidis et al., J. Appl. Phys. 99, 013307 (2006)]. TRIM simulations in combination with deposition rate experiments as a function of pulse width using Cu, W, and Ti as target materials reveal predominantly self-sputtering during Cu depositions. For W as well as Ti discharges, Ar contributes significantly more to sputtering, which may be explained by the low metal-self-sputtering yield. HPPMS deposition rates during reactive sputtering are reported to be comparable or even larger compared to DC magnetron sputtering rates [Wallin and Helmersson, Thin Solid Films in press]. Target erosion rate measurements for an HPPMS discharge exhibit two orders of magnitude larger erosion rates compared to DC magnetron sputtering.

10:40am **SE+PS-FrM8 Effects on Thin Film Growth Due to Anomalous Transport in High Power Impulse Magnetron Sputtering**, ***D. Lundin**, P. Larsson, E. Wallin,* Linköping University, Sweden*, M. Lattemann,* TU Darmstadt and Forschungszentrum Karlsruhe GmbH, Germany*, N. Brenning*, Royal Institute of Technology, Sweden*, U. Helmersson*, Linköping University, Sweden

In this study, the effect of a previously reported anomalous transport[1] on thin film growth in high power impulse magnetron sputtering (HiPIMS) has been investigated for the case of a planar circular magnetron. It was found that a large fraction of ions are transported radially outwards in the vicinity of the cathode, across the magnetic field lines, leading to enhanced deposition rates directly at the side of the cathode (on a substrate oriented perpendicular to the target surface). An important consequence of this type of mass transport parallel to the target surface is that the fraction of sputtered material reaching a substrate placed directly in front of the target is substantially lower in HiPIMS compared to conventional direct current magnetron sputtering (dcMS). This would help to explain the lower deposition rates generally observed for HiPIMS compared to dcMS. Moreover, time-averaged mass spectrometry measurements of the energy distribution of the cross-field transported ions were carried out. The measured distributions show a direction-dependent high-energy tail, which can be explained by an increase in the azimuthal force on the ions, exerting a volume force on the ions tangentially outwards from the circular race track region. These results are in agreement with predictions as well as recent modeling results of the anomalous transport mechanism.

[1] D. Lundin, U. Helmersson, S. Kirkpatrick, S. Rohde, and N. Brenning, Plasma Sources Sci. Technol. 17, 025007 (2008).

11:00am **SE+PS-FrM9 High Power Impulse Magnetron Sputtering of Ti-Si-C Multifunctional Thin Films**, ***M. Samuelsson**,* Linköping University, Sweden*, H. Högberg, H. Ljungcrantz,* Impact Coatings, Sweden*, U. Helmersson*, Linköping University, Sweden

Nanocomposite Ti-Si-C thin films grown by dc-magnetron sputtering (dcMS) are interesting for many applications, such as in electrical contacts. This is due to a property envelope including low contact resistance, ductility and hardness that can be combined. Other areas of applications are also suggested, which call for increased possibility to design the material for specific needs. A promising deposition technique is high power impulse magnetron sputtering (HiPIMS), which offers a high degree of ionization of the sputtered material not found in conventional dc-magnetron sputtering. Growth from ions instead of neutrals is likely to further increase the possibility of designing the film microstructure and thereby the properties. In this study we have investigated sputtering from a Ti_3SiC_2 target by HiPIMS and compared the technique with dcMS. The techniques have been compared for different process pressures and substrate bias voltages using a pilot plant deposition system under production like conditions. The results show that the obtained HiPIMS growth rate was approximately 13% of that of dcMS for comparable average powers. Further studies employing SEM, TEM, XRD measurements, surface resistivity and film adhesion will be presented.

11:20am **SE+PS-FrM10 Modulated Pulse Power Deposition of Aluminum Oxide Nanometer Scale Multilayer Films**, ***R. Chistyakov**,* Zond Inc.*, B. Abraham,* Zpulser LLC*, W.D. Sproul,* Reactive Sputtering, Inc.*, J.J. Moore, J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a versatile high power pulse magnetron sputtering technique in which there can be multiple voltage steps within a pulse. Different levels of applied voltage in the same voltage pulse will generate different power levels for the magnetron discharge. Usually each pulse shape has a weakly ionized plasma (low power magnetron discharge) step that was generated first, and then the second stage that has a strongly ionized plasma (high power magnetron discharge) by applying a voltage increase to the cathode. These arbitrary voltage pulse shapes can be used within a given deposition run to form multilayer film structure. Therefore every layer can be sputtered with a different voltage pulse shape. In this study, two different voltage pulse shapes were selected. The first pulse had a shorter duration that the second pulse, but by varying the repetition rate the same average power could be delivered during the sputtering of each layer. The peak power applied to the plasma was greater during the second pulse, which meant that a greater amount of energy was applied to the process during the peak power phase of the second pulse. The difference in the applied energy between the two MPP pulse shapes was used during the reactive sputter deposit of aluminum oxide films . This two-pulse approach did produce a nanometer scale layering of the aluminum oxide coatings, which was observed in a scanning electron microscope. The thickness and structure of each nanometer scale layer was controlled by varying the output voltage pulse shape of the MPP plasma generator and deposition time. The layering of the aluminum oxide affected not only the structure of the films, but it also affected the mechanical properties of the films. The film structure, orientation, and mechanical properties were analyzed and measured, and the results of the film property measurements will be presented.

11:40am **SE+PS-FrM11 The Specification and Optimization of HIPIMS Power Supply Parameters**, *D. Ochs,* Huettinger Electronics GmbH, Germany*, P. Ozimek,* Huettinger Electronics Sp. z.o.o., Poland*,* ***A.G. Spencer***, Alacritas Consultancy Ltd., UK

HIPIMS is a rapidly emerging technique for surface modification. It is well know the improvements in surface properties that can be acheived (in particular in mechanical properties). What is less well known is how to specify and operate the HIPIMS power supply. There are many aspects of the HIPIMS power supply that need to be specified at time of purchase, and adjusted for process optimization (average power, pulse power, pulse frequency, pulse length). Usually HIPIMS users are upgrading from a sputtering or evaporation process. These new HIPIMS parameters are therefore unfamiliar. This paper details the effects of each of these parameters, gives examples, and guidance on specifying a HIPIMS power supply.

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Mills, C.A.: NM+EM+PS+NS+NC-ThM5, 27
Millunchick, J.M.: NM+EM+PS+NS+NC-ThM6, **28**
Miron, C.: PS-ThP9, **38**
Mishra, B.: SE+PS-FrM5, 44
Mitamura, K.: PS-ThP6, 37; PS-ThP8, 38
Miura, N.: PS1-ThA8, **33**
Miwa, K.: PS1-WeA8, **23**
Miyake, M.: PS2-FrM7, 43
Moon, C.S.: PS-TuP3, **12**
Moore, J.J.: SE+PS-FrM10, 45; SE+PS-FrM4, 44; SE+PS-FrM5, **44**
Morgan, M.M.: PS1-WeM12, **19**
Mori, T.: PS-ThP8, **38**; PS-TuM10, **6**
Morikawa, Y.: PS2-FrM8, **43**
Morris, D.: NM+EM+PS+NS+NC-ThM6, 28
Morud, M.: PS-TuP25, 16
Mráz, S.: SE+PS-FrM6, 45
Muniz, A.R.: PS1-WeM3, 17
Murakami, Y.: PS2-ThM11, **32**
Murayama, T.: PS2-FrM8, 43
Musinski, L.: NM+EM+PS+NS+NC-ThM6, 28

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Na, B.-K.: PS-ThP13, 39
Nagahata, K.: PS1-FrM10, 42; PS-MoM5, 1
Nagai, M.: PS1-ThA9, 34
Nagaoka, T.: PS-TuP19, **15**; PS-TuP20, 15
Nakakubo, Y.: PS1-WeM4, **17**
Nakano, T.: PS1-WeM9, 18
Nakatani, T.: PS-TuP2, 12
Nealey, P.F.: BO+PS+AS+BI+SS-TuA8, 7; PS1-WeA12, 24
Negishi, N.: PS2-FrM7, **43**
Nest, D.G.: NM+EM+PS+NS+NC-ThM12, 28; PS-TuA10, 11; PS-TuA8, 10; PS-TuA9, **10**
Neumann, M.J.: PS2-WeA2, 24
Nicholas, R.J.: EN+EM+NS+PS-TuA5, 9

Niemi, K.: PS-TuP21, **15**
Nihey, F.: PS1-FrM8, 41
Nikles, D.E.: NM+PS+AS-WeA12, 22
Nishi, Y.: PS1-FrM1, 40; PS1-FrM2, 40
Nishizuka, T.: PS-TuM10, 6
Nisol, B.: PS-TuP9, **13**
Novikova, T.: PS2-ThA5, 35
Nozawa, T.: PS2-ThA7, 35; PS-TuM10, 6

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Ochs, D.: SE+PS-FrM11, 45
O'Connell, D.: PS1-ThA3, **33**
Oehrlein, G.S.: NM+EM+PS+NS+NC-ThM12, 28; NM+EM+PS+NS+NC-ThM4, 27; PS1-FrM4, 40; PS-MoA5, **3**; PS-TuA10, 11; PS-TuA8, 10; PS-TuA9, 10
Ohba, T.: PS1-ThA1, **33**
Ohsawa, Y.: PS2-ThA7, 35
Ohta, H.: PS1-WeM4, 17; PS-TuP19, 15; PS-TuP20, **15**; PS-TuP24, 16
O'Neill, L.: PS1-ThM10, 30
Ono, K.: PS1-WeM4, 17; PS-TuP19, 15; PS-TuP20, 15; PS-TuP24, 16
Oshima, K.: PS-MoM5, 1
Oubensaid, E.H.: PS1-FrM6, 41
Oyama, M.: PS2-FrM7, 43
Ozimek, P.: SE+PS-FrM11, 45

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Palumbo, F.: PS2-ThA11, 36
Pang, C.: PS-TuP7, 13
Pappas, D.D.: PS1-ThM9, **29**; PS-TuP4, 12
Paraschiv, V.: PS-TuM2, 5
Pargon, E.: PS1-WeA10, **23**; PS1-WeA3, 23; PS-TuM9, 6
Park, E.: PS-TuP25, **16**
Park, H.: PS-ThP1, 37
Park, K.: PS-TuP7, 13
Park, M.: PS-ThP1, 37
Park, Y.J.: PS1-ThM12, 30
Partlow, M.: PS2-WeM1, 19
Patriarche, G.: PS2-FrM1, 42
Patz, R.: PS-MoM8, 2
Pease, S.: PS-TuP5, 12
Peeters, F.J.J.: PS1-WeM1, 17
Pender, J.: PS-MoM8, 2
Penso-Blanco, G.: NM+EM+PS+NS+NC-ThM3, 27
Pereira, J.: PS1-FrM6, **41**
Pereira-Medrano, A.G.: BO+PS+AS+BI+SS-TuA5, 7
Perrin, F.: NM+EM+PS+NS+NC-ThM11, 28
Peterson, J.J.: NM+PS+AS-WeA11, **22**
Phaneuf, R.: NM+EM+PS+NS+NC-ThM12, 28; PS-TuA9, 10
Pi, X.-D.: NM+PS+AS-WeA1, 21
Pichon, L.E.: PS1-FrM6, 41
Pipino, A.C.R.: PS1-WeM1, 17
Poirier, J.S.: PS1-WeA1, 22
Poleunis, C.: PS-TuP9, 13
Porcar, L.: NM+PS+AS-WeA12, 22
Posseme, N.: PS-MoM1, 1; PS-MoM3, 1; PS-MoM7, 2; PS-MoM9, **2**
Potocký, Š.: PS1-ThM6, **29**
Pribyl, P.: PS1-ThA5, 33
Puttaswamy, M.: PS2-ThA9, **36**

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Raju, R.: PS2-WeA11, 26; PS-ThP2, **37**
Ramaswamy, K.: PS2-WeM10, 20; PS2-WeM4, 19
Ramos, R.: PS-TuA11, 11
Ranjan, A.: PS1-ThA7, **33**
Ranson, P.: PS1-FrM6, 41
Rauf, S.: PS2-ThM2, 30; PS2-ThM3, 31; PS2-WeM10, 20; PS2-WeM3, **19**; PS2-WeM4, 19; PS-TuM11, 6
Rauter, F.: BO+PS+AS+BI+SS-TuA10, 8
Ray, M.A.: PS1-ThM5, 29
Reed, D.: NM+PS+AS-WeA12, 22
Reniers, F.: PS1-FrM9, 41; PS-TuP9, 13
Reshetnyak, E.N.: PS2-WeM11, 20
Rhallabi, A.: PS-TuA12, **11**
Richards, D.N.: PS2-ThA3, 34
Ritter, A.: PS2-ThA8, 35
Ritz, E.: PS2-WeA2, **24**
Roark, C.: PS-TuP23, 16
Rochat, N.: NM+EM+PS+NS+NC-ThM11, 28
Roche, G.: PS1-ThA11, **34**
Rockett, A.: EN+EM+NS+PS-TuA10, 9
Rodriguez, M.A.: NM+PS+AS-WeA11, 22
Rogers, J.: NM+EM+PS+NS+NC-ThM1, 27
Rossi, F.: BO+PS+AS+BI+SS-TuA11, 8; NM+EM+PS+NS+NC-ThM5, 27
Rothe, R.: PS-TuP18, 15
Rowe, D.: NM+PS+AS-WeA1, 21
Ruiz, A.: NM+EM+PS+NS+NC-ThM5, **27**
Rumphorst, R.F.: PS2-WeA5, 25
Rusu, C.: PS2-FrM5, **43**
Ruzic, D.N.: PS2-WeA11, 26; PS2-WeA2, 24; PS-ThP2, 37
Ryu, S.H.: EN+EM+NS+PS-TuA3, **9**; NM+PS+AS-WeA3, 21

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Sadeghi, N.: PS1-ThA2, 33; PS1-ThM1, 28; PS-TuA11, 11
Saito, N.: PS1-ThM6, 29; PS-ThP6, 37; PS-ThP7, 38; PS-ThP8, 38; PS-ThP9, 38
Saito, R.: PS-MoM5, 1
Salim, M.: BO+PS+AS+BI+SS-TuA5, 7
Samitier, J.: NM+EM+PS+NS+NC-ThM5, 27
Samuelsson, M.: SE+PS-FrM9, **45**
Samukawa, S.: PS1-FrM5, 40; PS1-FrM8, 41; PS1-WeA11, 24; PS2-WeA3, 25
Sasaki, K.: PS1-WeA8, 23
Sasaki, M.: PS-TuM10, 6
Sato, Y.: PS1-FrM8, 41
Saussac, J.: PS2-ThM10, **32**
Sawin, H.H.: PS-TuA3, **10**; PS-TuA5, 10
Scarpa, G.: NM+EM+PS+NS+NC-ThM3, 27
Schaper, L.: PS1-ThM10, 30
Schmitz, S.: PS-MoM10, 2
Schneider, J.M.: SE+PS-FrM6, 45
Schultz, B.D.: PS1-ThM5, **29**
Sekine, M.: PS1-FrM3, 40; PS-TuP3, 12
Selinder, T.I.: SE+PS-FrM3, 44
Seman, M.T.: PS2-ThA3, 34
Seong, D.-J.: PS-ThP13, 39
Setsuhara, Y.: PS-TuP3, 12
Shamiryan, D.: PS-TuM2, **5**
Sheng, J.: EN+EM+NS+PS-TuA4, 9
Shin, H.: PS2-WeA11, 26; PS-ThP2, 37
Shin, Y.-H.: PS-ThP13, 39
Shindo, H.: PS1-ThA10, **34**; PS2-WeM6, 20
Shinohara, M.: PS-TuP2, **12**
Shir, D.: NM+EM+PS+NS+NC-ThM1, **27**
Shiratani, M.: PS-TuP3, 12
Shoeb, J.: PS-MoA9, 4; PS-TuP17, **14**
Shohet, J.L.: PS1-FrM1, **40**; PS1-FrM2, 40; PS-ThP10, 38
Siebentritt, S.: EN+EM+NS+PS-TuA8, **9**
Sikorski, E.M.: PS-TuA2, 10
Silterra, J.: PS2-WeM1, 19
Singh, T.: PS1-WeM3, 17
Sirard, S.: PS1-WeA2, 22; PS2-WeM5, 19
Smekalin, K.: PS-MoA2, 3
Smith, D.: PS2-WeM1, 19
Smithe, D.: PS-TuP23, **16**
Snyders, R.: SE+PS-FrM6, 45
Sobolewski, M.A.: PS2-WeA4, **25**
Soles, C.L.: NM+EM+PS+NS+NC-ThM4, 27
Sparks, T.: PS-MoM10, 2
Spencer, A.G.: SE+PS-FrM11, **45**
Sprinkle, M.: NM+PS+AS-WeA11, 22
Sproul, W.D.: SE+PS-FrM10, 45; SE+PS-FrM4, **44**; SE+PS-FrM5, 44
Srinivasan, M.: PS2-WeM5, 19
Stafford, C.M.: NM+EM+PS+NS+NC-ThM4, 27
Stafford, L.: PS1-WeA1, **22**; PS1-WeA2, 22; PS2-WeM9, 20
Stillahn, J.M.: PS1-WeM11, **18**
Stoltz, P.: PS-TuP23, 16
Stout, P.J.: PS-TuM11, 6
Strawhecker, K.E.: PS1-ThM9, 29
Strel´nitskij, V.E.: PS2-WeM11, **20**
Strobel, S.: NM+EM+PS+NS+NC-ThM3, **27**
Su, W.: PS2-FrM4, 43
Sundararajan, R.: PS-ThP4, 37
Sung, D.: PS-ThP1, 37
Suu, K.: PS2-FrM8, 43
Suzuki, A.: PS-MoM2, **1**

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Tachibana, K.: PS1-ThM3, **29**
Tajima, K.: PS1-FrM5, 40
Takada, N.: PS1-WeA8, 23
Takai, O.: PS1-ThM6, 29; PS-ThP6, 37; PS-ThP7, 38; PS-ThP8, 38; PS-ThP9, 38
Takashima, S.: PS-MoM5, 1
Takeda, K.: PS1-FrM3, 40; PS-MoM5, **1**; PS-TuP3, 12
Takizawa, T.: PS1-FrM10, 42
Tanaka, Y.: PS2-ThA7, 35
Tatsumi, T.: PS1-FrM10, 42; PS2-WeA3, 25; PS-MoM2, 1; PS-MoM5, 1
Taylor, K.: PS-TuP25, 16
Taylor, M.: BO+PS+AS+BI+SS-TuA1, 7
Thomas, O.: PS2-ThA1, 34
Thorgrimsson, C.: PS1-ThA9, 34
Tileli, V.: NM+PS+AS-WeA11, 22
Ting, Y.H.: BO+PS+AS+BI+SS-TuA8, 7; PS1-WeA12, **24**; PS1-WeM2, 17
Titus, M.J.: PS2-WeA1, **24**
To, B.N.: PS-TuA2, 10
Todorow, V.: PS2-WeM10, 20
Tohji, K.: PS1-FrM8, 41
Tornow, M.: NM+EM+PS+NS+NC-ThM3, 27
Touzeau, M.: PS1-ThA2, 33
Trevino, K.J.: PS-TuP6, **12**
Tsai, C.-H.: PS-ThP5, 37
Tummala, R.: PS2-FrM9, 43
Turkot, R.: PS-TuM5, **5**

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Uchida, S.: PS-MoM5, 1
Ueda, H.: PS2-ThA7, **35**
Ueda, Y.: PS1-WeM4, 17
Um, D.-S.: PS-TuP10, 13; PS-TuP11, 13; PS-TuP12, **14**; PS-TuP13, 14; PS-TuP15, 14
Upadhyaya, G.S.: PS1-FrM1, 40; PS-ThP10, **38**
Urbas, A.M.: PS2-FrM4, 43
Urquhart, A.J.: BO+PS+AS+BI+SS-TuA1, 7
Ushakov, A.: PS-ThP1, 37

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Vallier, L.: PS-MoM3, 1; PS-MoM7, 2; PS-TuM9, 6
Valsesia, A.: BO+PS+AS+BI+SS-TuA11, 8; NM+EM+PS+NS+NC-ThM5, 27
van de Sanden, M.C.M.: EN+EM+NS+PS-TuA1, **8**; PS1-WeM1, 17; PS1-WeM5, 18; PS2-WeA5, 25
Vandencasteele, N.: PS1-FrM9, **41**
Vandervelde, T.E.: EN+EM+NS+PS-TuA4, 9
Vasilyev, V.V.: PS2-WeM11, 20
Vegh, J.J.: NM+EM+PS+NS+NC-ThM12, 28; PS-TuA9, 10
Végh, J.J.: PS-TuA1, **9**
Vempaire, D.: PS1-ThA2, 33
Vermande, E.: NM+EM+PS+NS+NC-ThM11, 28
Verove, C.: PS-MoM1, 1; PS-MoM9, 2
Villani, M.L.: NM+EM+PS+NS+NC-ThM11, 28
Vitale, S.A.: PS-TuM1, **5**

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Wada, A.: PS1-FrM8, **41**

Wallin, E.: SE+PS-FrM3, **44**; SE+PS-FrM8, 45
Walton, S.G.: NM+EM+PS+NS+NC-ThM4, 27; PS-TuP4, **12**; PS-TuP8, 13
Wang, D.: PS-TuA10, 11; PS-TuA9, 10
Wang, M.: PS-MoA9, 4; PS-TuP14, **14**
Waskoenig, J.: PS-TuP21, 15
Wei, D.: PS1-WeA2, 22
Weilnboeck, F.: NM+EM+PS+NS+NC-ThM12, 28; PS-TuA10, **11**; PS-TuA8, 10; PS-TuA9, 10
Wendt, A.E.: BO+PS+AS+BI+SS-TuA8, **7**; PS1-FrM7, 41; PS1-WeA12, 24; PS1-WeM2, 17
Willson, G.: NM+EM+PS+NS+NC-ThM12, 28; PS-TuA9, 10
Wolden, C.A.: PS2-ThA3, **34**; PS2-ThA4, 35
Woo, J.-C.: PS-TuP11, 13; PS-TuP15, 14
Wright, P.C.: BO+PS+AS+BI+SS-TuA5, 7
Wu, C.Y.: PS2-WeA12, **26**
Wu, Z.: SE+PS-FrM5, 44

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Xue, J.: PS1-ThM2, **29**

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Yagisawa, T.: PS2-ThM4, 31; PS-TuM3, **5**
Yamamoto, H.: PS1-FrM3, **40**
Yang, C.: EN+EM+NS+PS-TuA3, 9; NM+PS+AS-WeA3, **21**
Yang, W.K.: PS-ThP11, 39
Yang, X.: PS-TuP13, **14**
Yang, Y.: PS2-ThM1, **30**; PS-MoA9, 4
Yano, H.: PS1-FrM5, 40
Yasuhara, S.: PS1-FrM5, 40
Yatsuda, K.: PS1-WeA9, 23
Ye, J.: PS2-WeM1, 19
Yin, Y.: PS-MoM10, **2**
Yokogawa, K.: PS2-FrM7, 43
Yoo, W.J.: EN+EM+NS+PS-TuA3, 9; NM+PS+AS-WeA3, 21; PS2-FrM10, 44
Yoshimaru, M.: PS1-FrM5, 40
You, S.J.: PS-ThP13, 39

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Zenasni, A.: PS-MoM1, 1
Zhang, C.: PS-MoM8, 2
Zhang, H.: PS-TuP1, **12**
Zhang, Y.: PS-TuA2, **10**
Zheng, J.: PS1-WeM1, **17**
Zhou, K.: PS-MoM8, 2
Zhou, Y.: PS-MoM8, 2
Zhu, H.: PS2-WeM1, 19