Plasma Science and Technology
Room: A1 - Session PS1-MoM

Advanced Interconnect Etch
Moderator: M. Armacost, Applied Materials, Inc.

8:20am **PS1-MoM1 Modification Mechanisms of Porous Low-k SiOCH Film during Plasma Ashing Processes**, ***K. Kurihara***, *T. Imamura, K. Yamamoto, H. Hayashi, Y. Nakasaki*, Toshiba Corp., Japan **INVITED**

Porous low-k SiOCH materials are being introduced in order to realize highly reliable interconnects for sub 32 nm node LSI. There are still several problems regarding its use. One of the problems is the damage to low-k materials during etching and ashing processes. During resist ashing process the loss of hydrophobic groups in the pore leads to the uptake of water into the film and results in an increase in k value. To overcome this issue, two approaches are considered. In one approach, the low-k material itself becomes resistant to the plasma processes. In the other, the low-damage plasma processes are developed. The collaboration of both approaches is probably necessary to achieve interconnection for future device generations. We studied the above two issues from the viewpoint of fundamental mechanisms. Concerning the former issue, we have examined the dependence of the plasma resistance of SiOCH films on the film structure, which contained the methylene-bridge (Si-CH_2-Si) and/or the methyl groups. It was found that the decrease in the amount of carbon in the SiOCH film containing only methyl groups is larger than that in the film containing methylene bridges. Concerning the latter issue, we have investigated the mechanism of ashing process using CO_2 plasma. It was found that a densified layer was formed at the outermost surface of the SiOCH film during ashing, and the layer plays an important role in the control of water absorption into the film. This ashing process resulted in lower damage to the SiOCH film compared with O_2 or N_2/H_2 plasmas.

9:00am **PS1-MoM3 Oxygen Plasma and Radical Interactions with Ultralow-K Organosilicates; Fundamental Damage Mechanisms**, ***J. Kelber***, *S. Behera, S. Manandhar, S. Gaddam*, University of North Texas

Exposure of ultralow-k organosilicate ("SiCOH") materials to oxygen plasma induces methyl group abstraction and other changes leading to significant increases in k value. We present ex situ FTIR and in situ XPS data for O_2 plasma and thermal ($E_{kinetic} < \sim 0.1$ eV) electronic ground state atomic O (thermal $O(^3P)$) interactions with SiCOH films. The data yield new insight concerning the fundamental mechanisms and kinetics of oxygen plasma-induced CH_3 abstraction, and how these are affected by organosilicate pore structure. FTIR measurements indicate that methyl group abstraction kinetics in the presence of a direct O_2 plasma are diffusion-dominated, and that this diffusion is directly related to SiCOH diffusivity (pore interconnectedness) rather than total pore volume. Pre-treatment of a high porosity/high diffusivity material with He plasma prior to O_2 plasma exposure sharply limits CH_3 abstraction in a manner similar to that exhibited by a vicinal high porosity/low diffusivity material—evidence that He pretreatment results in closure of pore channels. Exposure to $O(^3P)$ from a thermal source (1300 K) results in changes in FTIR spectra similar to exposure to O_2 plasma, indicating that thermal $O(^3P)$ is a major reactant in the diffusion-dominated CH_3 abstraction mechanism. In situ XPS analysis of thermal $O(^3P)$/organosilicate interactions indicate that carbon loss and O/OH incorporation in the organosilicate surface region occur *concurrently*; i.e., Si-C bond scission and Si-O formation are related processes resulting from interaction with $O(^3P)$. This conclusion is supported by recent ab initio DFT-based molecular simulation (AIMDS) results recently reported by Jincheng Du and co-workers (Chaudhari, et al., submitted) that also indicate energy barriers to O/SiCOH interactions are extremely trajectory-sensitive, thus providing a rationale for the experimentally indicated O diffusion mechanism. The experimental and theoretical data also provide insight concerning O interactions with other Si/C based materials, such as SiC, and the implications of this work for processing of SiC will be discussed.

Acknowledgments: This work was supported by the Semiconductor Research Corporation under task ID 1862.001 and by the Robert Welch Foundation under grant B-1356. The authors thank Dr. G. A. Antonelli for providing samples and for useful discussions.

9:20am **PS1-MoM4 Synergistic Damage Effects of Vacuum Ultraviolet Photons and O_2 in SiCOH Ultra-Low-*k* Dielectric Films**, ***J. Lee***, *D.B. Graves*, University of California-Berkeley

Damage originating from plasma processing is a persistent problem with porous ultra-low-*k* dielectric films, such as SiCOH. Although most of the proposed mechanisms of plasma-induced damage focus on the role of ion bombardment and radical attack, vacuum ultraviolet (VUV) photons have been shown to play a role in bond modification of this material [1]. Using a vacuum beam apparatus with a calibrated VUV lamp, we show that 147 nm VUV photons cause bond scissioning in SiCOH, resulting in subsequent, post-exposure adsorption and reaction of water vapor from the atmosphere. Furthermore, the level of damage increases significantly under simultaneous exposure to VUV photons and O2. The role of photodissociation (and O radical formation) is shown to be negligible for the experimental conditions. The vacuum beam photon exposures are representative of typical plasma processes. Fourier-transform infrared (FTIR) spectroscopy implies that O2 itself reacts with photo-generated Si radical sites, replacing scissioned Si-C bonds with Si-O bonds (and ultimately SiOH groups) and making the surface more hydrophilic than with photon exposure alone. The present results demonstrate that VUV photo-generated surface reactions can be potent contributors to ultra-low k dielectric SiCOH film plasma-induced damage, and suggest that they could play analogous roles in many other plasma-surface interactions.

[1] Jinnai, B. et al., Damage Mechanism in low-dielectric (low-*k*) films during plasma processes. *Journal of Vacuum Science & Technology B*, 2008, 26(6): p. 1926.

9:40am **PS1-MoM5 Sidewall Modification of Porous SiOCH Ultra Low k Materials Induced by Reducing and Oxidizing Post Etching Plasma Treatments**, ***R. Bouyssou***, *T. Chevolleau*, CNRS-LTM, FRANCE, *N. Posseme, T. David, Ch. Licitra,* CEA-LETI-MINATEC, France, *A. Ostrowsky, C. Verove,* STMicroelectronics, France, *O. Joubert*, CNRS-LTM, France

From 32 nm interconnect technology node and below, porous SiOCH (p-SiOCH) materials presenting a porosity higher than 25% and a dielectric constant lower than to 2.5 are introduced. However the porosity introduction leads to complex integration issues. One of them is the high sensitivity of porous materials to radical species generated by the plasma during etching and ashing processes. An other serious issue brought by the porosity is the possibility of metal diffusion into the dielectric during conformal metallic barrier deposition. In order to surmount those issues, the optimization of post etching plasma treatments (PET) using reducing and oxidizing chemistries present some interest since such treatments can be efficient not only as post-etching cleaning processes of the sidewall patterns and reactor walls but also potentially as "pore sealing-like" processes to prevent metal barrier diffusion.

In this work, plasma induced modifications of p-SiOCH sidewalls have been investigated using volume and surface analyses techniques such as ellipsometric porosimetry (EP), infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and HF decoration techniques (resin encapsulation followed by a HF dip). After p-SiOCH patterning (porosity of 27% and k=2.35) using a TiN hard mask, p-SiOCH structures are exposed to in situ PET using different chemistries (NH_3, H_2, CH_4 or O_2) in a dual frequency capacitive reactor. The NH_3, H_2, CH_4 or O_2 treatments are first optimized on blanket wafers with the objective to minimize p-SiOCH modifications, i.e mainly methyl depletion and moisture uptake.

After etching in CF_4 / C_4F_8 / N_2 / Ar plasma, chemical topography analyses by XPS show the presence of a fluorocarbon (FC) layer on the p-SiOCH sidewalls. The FC layer is always removed whatever the post-etching plasma treatments and the surface of p-SiOCH sidewalls trenches is carbon and nitrogen rich after the CH_4 based PET and SiOF like after the NH_3, H_2 and O_2 PETs. The HF decoration technique and EP (with water used as solvent) show that the modified surface of the sidewalls is hydrophilic (thickness of the modified sidewall layer is between 15 and 20 nm) after the NH_3, H_2 and O_2 PETs while only a slight modification of the pattern sidewalls is detected after CH_4 based PET (less than few nanometers). The mechanisms leading to the p-SiOCH sidewall modification (pore sealing, methyl depletion...) induced by the plasma will be analyzed through the EP and FTIR analyses . The capabilities of such post-etching plasma treatments to prevent the barrier diffusion into p-SiOCH will be also discussed.

10:00am **PS1-MoM6 Reaction Mechanism and Profile Evolution for Porous Low-*k* Dielectric Sealing by Combined He and NH_3 Plasma Treatment**, ***J. Shoeb***, Iowa State University, *M.J. Kushner*, University of Michigan

Porous dielectric materials offer lower capacitance that reduces RC time delay in integrated circuits. While porosity of the dielectric can be as high as 0.5, the pores open to the surface which are internally connected can offer pathways for reactive species to enter into the porous network resulting in a degraded dielectric constant. The porous *low-k* materials are

typically SiOCH – silicon dioxide with carbon groups, principally CH_3, lining the pores. Reactions with the CH_x groups can increase the *k* value of the material. To maintain the *low-k* value of porous dielectrics, sealing of the surface pores is desirable. Treatment of the porous material with successive He and NH_3 plasmas has been successful in sealing the pores[1]. The He plasma can break Si-O bonds creating dangling bonds on the SiO_2 surface while knocking off H atoms from CH_3 group which is connected to Si of SiO_2 by a Si-C bond. This creates more reactive CH_x (x = 1,2) species without significant damage to the substrate. Successive NH_3 plasma treatment seals the pore as NH_x (x=0,1,2) species passivate previously produced Si forming Si-N bonds and reactive CH_x groups adsorbing NH_x species to form C-N bonds. A reaction mechanism has been developed for the sealing of a porous carbon doped silica films (SiOCH) in sequentially applied He and NH_3/Ar plasmas. The HPEM (Hybrid Plasma Equipment Module) was employed to obtain the ion energy and angle distributions of reactive fluxes from inductively coupled plasmas. These are used as input to the MCFPM (Monte Carlo Feature Profile Module) with which profiles of the low-*k* materials after the plasma exposures are predicted. Results will be discussed, including validation with data from the literature, for the densification and sealing of pores as a function of pore radius, porosity, interconnectivity, bias voltage and plasma power.

1. A. M. Urbanowicz, et al., Electrochem. Solid-State Lett. **10**, G76 (2007).

* Work supported by Semiconductor Research Corp

10:40am **PS1-MoM8 Materials Interactions as a Challenge for BEOL RIE at 22nm Node and Beyond**, ***Y. Yin***, *J.C. Arnold,* IBM, *K. Zin, C. Chu, Y. Feurprier,* Tokyo Electron Limited, Japan, *Y. Mignot,* STMicroelectrics, *M. Sankarapandian, J. Chen, X. Liu*, IBM

As feature critical dimension (CD) shrinks toward the 22nm node and beyond, many problems become serious challenges for BEOL plasma patterning. Dimensionally, as pitch size reaches 100nm or below, pattern breakdowns due to resist delamination, mask wiggling and dielectric flopover have been observed. One of the root causes is the high Aspect Ratio (AR) of mask/dielectric lines. Two of the most significant mechanisms, mask flopover and dielectric flopover, occur during the plasma etching process. In the event of former, the soft organic materials in the litho stacks can bend over and lead to mask flopover when the AR is high. This flopover partially shadows the trench and forms distorted dielectric lines. In the later case, the dielectric lines themselves 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 flopover due to capillary forces. Pattern profile control during BEOL RIE is another major concern and needs to be addressed in order to improve product yield and reliability. In particular, low-k material sidewall damage and trench bottom roughening during RIE need to be improved for better profile control. Moreover, characterization of feature profiles at 22nm node and beyond is a significant challenge. In this paper, the RIE efforts on pattern wiggling/flopover, pattern profile control and profile characterization will be addressed.

This work was performed by the Research Alliance Teams at various IBM Research and Development facilities.

11:00am **PS1-MoM9 Challenges in Porous Ultra Low-k for 22nm Dual Damascene Trench Etch**, ***Q. Zhou***, *R. Patz, A. Darlak, J. Pender, M. Armacost,* Applied Materials, Inc., *C. Labelle,* GLOBALFOUNDRIES, *D. Horak*, IBM Research

The development of 32nm technology processes highlighted many issues associated with Ultra Low-K (ULK) material. The softness and porosity of ULK caused many challenges, such as etch front roughness and strip damage, requiring modifications to the etch chemistry, pressure regime and plasma density. This learning has been applied to the 22nm node but new issues have developed. As we go to sub-100nm pitch features, there appears to be a critical dimension where the microloading increases dramatically. Traditional methods of correcting this response, such as pressure, bias power and degree of polymerization modifications, are not as effective for these small feature sizes. Adding to the difficulty of solving this issue is the restriction put on the available process regime by other ULK concerns, e.g. etch front roughness, faceting, film damage, etc.. Microloading trends, and strategies for improving it, have been identified and will be presented. A second issue encountered at sub-100nm pitch involves multi-layer photoresist patterning. As feature size shrinks the aspect ratio of the masking material increases. If the aspect ratio is high enough, and the process conditions are not managed correctly, pattern flop-over has been observed. Proper management of the etch steps can help mitigate flop-over, but there is a limited process window. Some of the issues surrounding this phenomenon will be discussed.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:20am **PS1-MoM10 Sidewall Roughness Transfer during Advanced Interconnect Patterning: Impact of Masking Strategies and Plasma Etching Processes**, ***J. Ducote***, STMicroelectronics, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *T. Chevolleau,* LTM-CNRS, France, *A. Ostrovsky,* STMicroelectronics, France, *M. Guillermet,* CEA-LETI-Minatec, France, *F. Bailly,* STMicroelectronics, France, *E. Pargon, R. Inglebert,* LTM-CNRS, France, *C. Verove,* STMicroelectronics, France, *O. Joubert*, LTM-CNRS, France

As copper lines are continuously scaling down, the biggest issue we are facing today is the copper resistivity increase due to the scattering effect at the grain boundaries and surface. Recent study has proved that this behavior is potentially associated with the sidewalls roughness of the lines also leading to an increase of the time dependent dielectric breakdown [1].

Starting from an initial line width roughness (LWR) printed in the photoresist after the lithography step, we have investigated the impact of the etching chemistries on the LWR transfer in a damascene structure as a function of the hard mask strategy (metallic or organic).

To monitor the LWR variation, a three-dimensional critical dimensions-atomic force microscope (CD-AFM) from Veeco has been used. This technique allows reconstruction of the trench profiles of the patterns and measurement of the LWR along the trenches. However such analyses require the development of a specific protocol to determine the LWR after porous SiOCH integration in a dual damascene architecture.

In order to avoid any consumption or sticking of the AFM tip, it is mandatory i) to use a tip with a high stiffness and ii) to measure the LWR of the damascene structures after the etching and wet cleaning. The line width roughness measurements are performed on 100 scan lines over a scan length of 2 µm with a tip diameter of 100 nm and tip edge of 20nm, allowing a measurement accuracy of less than 1 nm.

We have investigated the impact of the two masking strategies investigated (titanium nitride (TiN) versus organic) and different etching chemistries (used for BARC open, TiN open and dielectric etching) on the LWR transfer by monitoring the LWR variation between LWR on photoresist trenches and LWR on p-SiOCH trenches.

No impact of the different chemistries investigated has been observed with a TiN hard mask. The initial LWR on the photoresist patterns (~6nm) remains almost constant after porous SiOCH lines etching. The comparison of the transfer of sidewalls roughness between a TiN and an organic mask will be also presented.

[1] E. Soda et al., JVSTB, 27(2), 2009, pp649

11:40am **PS1-MoM11 Post Etch Treatments as Solution to Limit or Prevent Residue Growth on Metallic Hard Mask after Porous SiOCH Etching in Fluorocarbon Based Plasma**, ***N. Posseme***, CEA-LETI-MINATEC, France, *R. Bouyssou, T. Chevolleau,* LTM-CNRS, France, *T. David,* CEA-LETI-MINATEC, France, *V. Arnal, C. Verove,* STMicroelectronics, France, *O. Joubert*, LTM-CNRS, France

For 45 nm interconnect technology node, porous SiOCH (p-SiOCH) materials are being introduced, leading to complex integration issues due to their high sensitivity upon etching and ashing plasmas exposure . Metallic hard mask (MHM) integration avoids exposure of the porous film to plasma stripping processes but generate its own issues such as metal contamination on patterned structures (leading to line and via opens, strongly impacting the yield performance).

In this work, we have investigated the efficiency of *in situ* post-etch plasma treatments (PET) such as NH_3, CH_4, O_2 and H_2 to limit or prevent residues formation.

First, the experiments have been performed on TiN blanket wafers deposited on 200 nm thick SiO_2 layers. The TiN layer has been exposed to conventional fluorocarbon (FC) based chemistry and PET in an industrial dual frequency capacitively coupled plasma etcher. Different analyses techniques such as scanning electron microscopy (SEM) and ex-situ x-ray photoelectron spectroscopy (XPS) have been used in order to analyze the presence of metal residues and have a better understanding of the residue formation mechanism .

After FC etching and atmosphere exposure, a huge density of residues is observed, correlated with the presence of significant fluorine concentration (33%) on the TiN surface. The mechanism of metallic residues formation on the metallic hard mask has been clearly identify as a reaction between fluorine and air moisture (forming HF acid) and the oxidized metal to form a metallic salt.

H_2, O_2, and NH_3 PET strongly reduce the density of residues by partially removing fluorine on the TiN surface (8-13%). With the CH_4 PET, no more residues are observed despite an important fluorine concentration (28%) remaining on the surface. The residue removal is explained by the formation of a thin carbon passivation layer on top of the TiN surface preventing reactions between fluorine and air moisture.

Furthermore, a complementary study has been performed on patterned wafers using trench first MHM integration with a PECVD p-SiOCH dielectric (porosity of 20%, k=2.5). The implementation of the post-etch plasma treatment show that the residues density on MHM strongly depends on the etching chemistry with H_2, O_2, NH_3 while with CH_4, the efficiency in preventing residues formation is not chemistry dependent. The implementation of such PETs using a MHM and a porous SiOCH has been successfully integrated with an improvement of the electrical performances.

Plasma Science and Technology
Room: A8 - Session PS2+PV-MoM

Plasma Processing for Photovoltaics
Moderator: T.A. Gessert, National Renewable Energy Laboratory

8:40am **PS2+PV-MoM2 Plasma Etching and Texturing of Multi-Crystalline for Silicon Solar Cells using Remote-Type Pin-To-Plate Dielectric Barrier Discharge**, ***J.B. Park***, *J.S. Oh, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

During the preparation of the wafers for the multi-crystalline silicon (mc-Si) solar cells, the mechanical saw damage induced during the slicing of mc-Si ingots into wafers needs to be removed by etching in addition to the texturing of the silicon surface for the increased light scattering. For the etching and texturing of the mc-Si substrates, isotropic wet processing by using alkaline or acid solution is generally applied, however, wet treatments are environmentally undesirable due to the large amount of chemicals used.

In this study, an atmospheric pressure plasma called "remote-type pin-to-plate DBD" was used for the application to the etching of the saw damage removal and texturing process of mc-Si to increase the processing rate by increasing the plasma density without damaging the substrate surface. Especially, the effect of additive gases such as NF_3 and O_2 to the N_2-based atmospheric pressure plasma on the etching and texturing characteristics of mc-Si was investigated.

The results showed that the addition of NF_3 up to 1 slm increased the mc-Si etch rate continuously by increasing the F radicals in the gas mixture. Furthermore, the addition of a certain amount of O_2 (400sccm) to the mixture of N_2(40 slm) /NF_3(1slm) increased the mc-Si etch rate further by showing the two times higher etch rate of mc-Si (749.6 nm/scan, 1meter/scan). Especially, the addition of O_2 to the N_2/NF_3 improved the surface morphology by increasing surface texturing and, by the addition of 600sccm O_2, the reflectance less than 20% could be obtained.

9:00am **PS2+PV-MoM3 Production of Crystalline Si Nanoparticles for Third Generation Photovoltaics using a Multi-Hollow Discharge Plasma CVD Method**, ***Y. Kawashima***, *H. Sato, K. Koga, M. Shiratani*, Kyushu University, Japan, *M. Kondo*, AIST, Japan

Novel solar cells employing multiple exciton generation (MEG) are attracting much attention as third generation solar cells of high efficiency above 20%. For the MEG, an energetic exciton is generated in a semiconductor nano-crystal by a high energy photon more than twice as large as the band gap of the nano-crystal. Subsequently, the energetic one produces another in the nano-crystal by the inverse Auger process [1]. An issue for realizing the MEG solar cells is production of size-controlled crystalline Si nanoparticles. We have produced crystalline Si nanoparticles of 1 nm in size using a multi-hollow discharge plasma CVD method [2]. For the multi-hollow discharge plasma CVD method, discharges are sustained in small hollows of 5 mm in diameter. Crystalline nanoparticles are nucleated and grow in the discharges of SiH_4+H_2 (>99.5%) and then they are transported to the downstream region by gas flow. Their size is limited up to a few nm in size due to a short gas residence time in hollows. Nanoparticles are collected by stainless mesh grids located at the downstream region. They are dispersed in methanol to measure their photoluminescence. The excitation laser wavelength is 244nm or 405nm. For 405nm light irradiation,the photoluminescence spectrum has a peak at 490nm (2.53eV), corresponding to the bandgap of the Si nanoparticles of 1 nm in size. For 244nm light irradiation, the spectrum has a 380nm (3.27eV) peak corresponding to recombination centers at their surface as well as a 484nm (2.56eV) peak corresponding to their bandgap. These experimental results demonstrate generation of excitons in the Si nanoparicles. Si nanoparticles produced may be applicable as a material for MEG solar cells. We also have measured absorption spectrum of Si nanoparticles dispersed in methanol. Si nanoparticles show stronger light absorption at the shorter wavelength (<250 nm). To realize MEG solar cells, fabricating nanoparticles of an optimaized size for MEG in large quantity is important.

[1] A.J.Nozik, Physica E **14**, (2002)115.

[2] T. Kakeya, Kazunori Koga, Masaharu Shiratani, Yukio Watanabe, Michio Kondo, The Solid Films, **506-507**, (2006)288.

9:20am **PS2+PV-MoM4 Novel Model-Based Sensor for Thin Film Deposition on Large Area Substrates**, *M. Klick*, Plasmetrex, Germany, ***L. Eichhorn***, *R. Rothe*, Plasmetrex

Large area plasma coating becomes more important with increasing diameter of semiconductor wafers and thin film Si solar cells. The layer characteristics as uniformity of films produced by capacitive RF plasmas depends on effects as the standing wave and skin effect.

A reduced plasma physical model in the novel sensor is used to describe special features of large area and capacitive RF plasmas. It involved dynamic electron effects by a fluid model for the plasma bulk and nonlinear mechanisms by a nonlinear sheath model - called it Nonlinear Extended Electron Dynamics (NEED).

It involves also the nonuniformity and nonlinearity of the plasma sheath in the front of the substrate electrode, large electrode area, and medium pressure. The model provides also the dependence of the Fourier spectrum of the local RF current on the plasma density and the electron collision rate. Only lower harmonics of the RF current can be observed at medium pressure (100 Pa – 1000 Pa). Depending on the amount of harmonics of the local RF current used, it can be utilized also to estimate important plasma parameters as the electron collision rate and the ratio of the excitation frequency to the resonance frequencies of the spatial modes is found to determine the nonuniformity caused by the standing wave. The skin depth can be estimated as well to show the influence on spatial distribution of the RF current.

The major advantage is the real time, robust, and non-intrusive characterization of large area plasmas. An additional feature is the easy calculation of the plasma sheath voltage distribution at the grounded counter electrode. Both is mandatory to understand and to control the deposition rate distribution in particular for large area RF plasmas. So cost-efficient virtual metrology can substitute partially the expensive and time intensive real metrology.

9:40am **PS2+PV-MoM5 Plasma Processing of Thin Silicon Films for Photovoltaic Applications**, ***A.H.M. Smets***, National Institute of Advanced Industrial Science and Technology, Japan and Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands, *T. Matsui, M. Kondo*, National Institute of Advanced Industrial Science and Technology, Japan **INVITED**

Hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) are thin film silicon phases which are generally deposited at low processing temperatures by means of plasma enhanced chemical vapour deposition (PECVD) using hydrogen diluted silane gas mixtures. The lattice of dense a-Si:H is best described by a vacancy rich network (1-2 %) which lacks any medium and long range order, whereas the lattice of μc-Si:H consists of crystalline silicon grains (few nm's up to microns) imbedded in to an amorphous network or tissue. One hot application of these films is the integration in to thin silicon film photovoltaic devices. In comparison to a-Si:H phase, the μc-Si:H phase has the advantage of an enhanced spectral response in the red part of the solar spectrum and a better opto-electronic stability under illumination.

Since the deposition of the μc-Si:H phase under low processing temperatures (~160-250 ^oC) is obtained by increasing the hydrogen dilution in a silane plasma, it is believed that additional flux of atomic hydrogen at the surface enhances crystalline relaxation of the silicon atoms in the lattice during growth.

With respect to photovoltaic applications of μc-Si:H, high quality material is classified as dense material without any significant post-deposition oxidation, as oxidation is linked to a reduction in the red response of the *p-i-n* solar device. This specific μc-Si:H phase has the following properties: 1) crystalline grains with a preferentially [220] oriented growth, 2) has no crystalline grain boundaries, as these internal surfaces have been identified as the location at which the unwelcome post-deposition oxidation occurs and 3) is deposited close to conditions in which the growth transfers from amorphous to microcrystalline.

In this contribution we will address in detail the material properties of μc-Si:H and its relation to its performance in solar cells, the growth mechanism of the μc-Si:H phase under plasma deposition conditions and the crucial role of the control of plasma processing in obtaining device grade material. Finally, we will discuss the upscaling of the deposition technology (high deposition rates over large areas), which is an important issue in substantially reducing the cost-price of thin silicon photovoltaic products. We will present the recently explored deposition regime at higher processing pressures (~5-25 Torr), which has a high potential to bring about this important breakthrough in the thin silicon film photovoltaic technology.

10:40am **PS2+PV-MoM8 Atomic Hydrogen Induced Defect Kinetics in Hydrogenated Amorphous Silicon: An In Situ Real Time Study**, ***M.C.M. van de Sanden**, F.J.J. Peeters,* Eindhoven University of Technology, The Netherlands*, J. Zheng,* Peking University, China*, I.M.P. Aarts,* ASML, The Netherlands*, A.C.R. Pipino,* Tanner Research*, W.M.M. Kessels*, 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 20-80 nm a-Si:H films were grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by thermal decomposition of silane on a hot filament. Measurements are performed over a temperature range of 80 – 200 ºC. The observed changes in the optical loss during H dosing of a-Si:H are attributed to the creation and healing of sub-gap Dangling Bond (DB) defect states and were measured with a sensitivity of ~ 10^{-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 decreases with temperature. 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. Due to their limited lifetime the created DB defects are identified as the result of H insertion into strained Si-Si bonds in the bulk material. Extensive kinetic modeling of this process is used to determine activation energies for the hydrogen-material interactions and DB formation in a-Si, which are of key importance in a-Si:H thin film solar cells. Moreover the implications of this study for Eley-Rideal type reactions on the surface and hydrogen exchange reactions in the bulk will be addressed.

11:00am **PS2+PV-MoM9 Hydrogen-dominated Plasma, Due to Silane Depletion, for Microcrystalline Silicon Deposition**, ***A.A. Howling**, R. Sobbia, Ch. Hollenstein*, EPFL Lausanne, Switzerland **INVITED**

Plasma conditions for microcrystalline silicon deposition generally require a high flux of atomic hydrogen, relative to SiH_x radicals, on the growing film. The necessary dominant partial pressure of hydrogen in the plasma is conventionally obtained by hydrogen dilution of silane in the flow inlet. However, a hydrogen-dominated plasma environment can also be obtained due to plasma depletion of the silane in the gas mixture, even up to the limit of pure silane inlet flow, provided that the silane depletion is strong enough. At first sight, it may seem surprising that the composition of a strongly-depleted pure-silane plasma consists principally of molecular hydrogen, without significant contribution from the partial pressure of silane radicals. The aim here is to bring some physical understanding by means of a zero-dimensional, analytical plasma chemistry model. The model is appropriate for uniform, large-area showerhead reactors as shown by comparison with results of three-dimensional numerical simulations. The SiH_x densities remain very low because of their rapid diffusion and surface reactivity, contributing to film growth which is the desired scenario for efficient silane utilization. Significant SiH_x densities due to poor design of reactor and gas flow, on the other hand, would result in powder formation wasting silane. Conversely, hydrogen atoms are not deposited, but associate on the film surface and re-appear as molecular hydrogen in the plasma. Therefore, in the limit of extremely high silane depletion fraction (>99%), the silane density falls below the low SiH_x densities, but only the H radical can eventually reach significant concentrations in the hydrogen-dominated plasma.

11:40am **PS2+PV-MoM11 Plasma Uniformity Measurements in a Scalable, Multi-Electrode, VHF/UHF Plasma Source**, ***D. O'Farrell**, A.R. Ellingboe, S. Linnane, C. Gaman*, Dublin City University, Ireland

The ability to deposit large area thin film amorphous silicon films using PECVD is of significant interest in a number of fields including photovoltaics and flat panel display. The desire to deposit larger area films faster has lead to a recent push towards the use of VHF/UHF frequencies which result in faster deposition rates but also result in significant film non-uniformities due to wavelength effects even over relatively small areas. Several methods have been employed in an attempt to overcome these non-uniformity issues but many barriers still exist when it comes to wide scale application. In this work a scalable, multi-electrode, VHF/UHF plasma source is described which aims to resolve these issues. Data is presented demonstrating plasma uniformity over the source for a series of powers, pressures and operating frequencies. Different operating regimes are discussed.

Advanced Surface Engineering
Room: C4 - Session SE2-MoM

Pulsed Plasmas in Surface Engineering
Moderator: J. Patscheider, EMPA, Switzerland

8:20am **SE2-MoM1 Industrialization of Metal Ion Sputtering**, ***R. Cremer***, KCS Europe **INVITED**

Since its introduction by Kouznetsov et al. in 1999, the HIPIMS technology has seen a remarkable rise in interest from both academic and industrial viewpoint. Although the high ionization of the plasma and the resulting advantages for industrial sputter applications have been verified more than a decade ago, industrial usage of the metal ion sputtering technology has been limited due to various technical drawbacks.

Only recently, a various number of authors have reported the overcome of the hitherto existing disadvantages of the technology like low deposition rate, biasing issues, arcing and reliability of the technology.

This paper gives an overview on the industrialization of metal ion sputtering in various applications. Special focus will be given to the comparison of ionization in different coating technologies like sputtering, metal ion sputtering, arc ion plating and thermionic arc evaporation. The paper will also comment on future options and limitations of industrial metal ion sputtering.

9:00am **SE2-MoM3 Structural and Mechanical Behavior of Fullerene-Like and Amorphous Carbon Nitride Thin Films Deposited by HPPMS**, ***S. Schmidt**, G. Greczynski,* Linköping University, Sweden*, E. Broitman,* Carnegie Mellon University*, L. Hultman*, Linköping University, Sweden

The structural and mechanical properties of fullerene-like (FL) and amorphous carbon nitride (CN_x) films were deposited using High power pulsed magnetron sputtering (HPPMS) in an industrial CC-800/9 CemeCon chamber and compared with films deposited by DC magnetron sputtering mode of operation.

Films of 1 µm and 2 µm thickness were grown on Si and steel substrates, respectively. Carbon nitride films were deposited via HPPMS from a high purity graphite target in an Ar/N_2 discharge at 400 mPa, the N_2 fraction varied from 0 to 0.5 and different substrate temperatures ranging from ambient temperature to 300°C were chosen. Furthermore, a novel HPPMS substrate pretreatment employing two HPPMS power supplies was used to optimize the adhesion of the films: the first power supply established the discharge; the second produced a pulsed substrate bias. The created Cr-plasma cleaned the substrate surface and formed a Cr-containing gradual interface into the substrate. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to study the microstructure of both, the films and the interfaces. The hardness and the elastic recovery of the CN_x films were measured using nanoindentation. A deposition process window is demonstrated for the growth of dense fullerene-like (FL) film structures consisting of curved, frequently intersecting, and highly in-plane oriented basal planes.

9:20am **SE2-MoM4 Effects of the Working Pressure and Pulse Parameters on the Ion Energy and Mass Distributions in Modulated Pulse Power Sputtering Plasma**, ***W.D. Sproul**,* Reactive Sputtering, Inc.*, J. Lin, J.J. Moore, B. Mishra,* Colorado School of Mines*, J.A. Rees,* Hiden Analytical Ltd, UK*, Z.L. Wu, J. Wang,* Colorado School of Mines*, R. Chistyakov, B. Abraham*, Zond/Zpulser

The modulated pulse power (MPP) sputtering technique is a variation of high power pulsed magnetron sputtering (HPPMS) that generates a high ionization density plasma by manipulating the pulse shape, intensity, and duration. In this study, the time-averaged ion energy and ion mass distributions of the MPP plasma generated during sputtering a metal Cr target in pure Ar at different working pressures, pulse frequencies, and the strong ionization periods were investigated. The MPP plasma was studied using an electrostatic quadrupole plasma mass spectrometer which was installed parallel to the target surface in a closed field unbalanced magnetron sputtering system. It was found that an increase in the working pressure led to an increase in the peak ion flux and a decrease in the high ion energy tail. An increase in both the gas and metal ion species was observed as the pulse frequency was increased using the same pulse shape. Additionally, the effects of different combinations of the weak and strong ionization durations on the ion energy distributions of the gas and metal ion species will be reported.

10:00am **SE2-MoM6 Effects of HiPIMS Plasma Transport on Thin Film Deposition**, ***D. Lundin***, Linköping University, Sweden, *N. Brenning, M.A. Raadu,* Royal Institute of Technology, Sweden, *U. Helmersson*, Linköping University, Sweden

A new exciting development of magnetron sputtering was achieved when introducing high power impulse magnetron sputtering (HiPIMS). HiPIMS is one of the most promising improvements of common IPVD techniques and is already making its way to industrial applications. The HiPIMS plasma generates large quantities of ions of the sputtered material due to a high plasma density, but also acceleration of the ions increasing the bombardment of the growing film without using a substrate bias voltage. Also observed is a lower deposition rate for HiPIMS than that obtained for conventional DC sputtering, using the same average power. In order to optimize the process, controlling ion acceleration and increasing deposition rate, the mechanisms for transport of charged particles in this type of plasma need to be known. In the present work, it is shown that the electron mobility across the magnetic field is enhanced by typically an order of magnitude during the HiPIMS discharge compared to DC magnetron sputtering. This cannot be explained by classical theory of diffusion and electrical conductivity or Bohm diffusion. The transport is directly reflected by an anomalously low azimuthal-to-discharge current ratio, $J_\varphi / J_D = 2$. On the microscopic scale, the anomalous transport can be shown to be mediated by observed azimuthal electric field oscillations in the lower hybrid range. Furthermore, new insights from experimental data and plasma discharge modeling will be presented, which show that a large fraction of the ionized species are attracted back towards the target, either by electric fields in the bulk of the plasma, or by the stronger local fields in the cathode sheath. In this context, it is demonstrated that the effect of the anomalously high electron mobility to reduce the bulk **E** field is important to understand and control. The study also verifies that the resistive friction force, $\mathbf{F}_{i,\varphi}$, associated with the anomalous resistivity, can accelerate the ions azimuthally, as is shown both indirectly from changes in the deposition patterns, and directly by mass spectrometry.

10:40am **SE2-MoM8 Deposition Rates of High Power Impulse Magnetron Sputtering: Physics and Economics**, ***A. Anders***, Lawrence Berkeley National Laboratory **INVITED**

Deposition by high power impulse magnetron sputtering (HIPIMS) is considered by some as the new paradigm of advanced sputtering technology, yet this is met with skepticism by others for the reported lower deposition rates, if compared to direct current (DC) sputtering of equal average power. In this contribution, absolute and relative (normalized) deposition rates are compared, and the underlying physical reasons for differences are discussed, including (i) ion return for self-sputtering, (ii) the less-than-linear increase of the sputtering yield with increasing ion energy, (iii) yield changes due to the shift of species responsible for sputtering, (iv) change in plasma impedance and sheath voltage, (v) changes in film density, (vi) noticeable losses in the switch module, (vii) changes of the magnetic balance and particle confinement of the magnetron due to self-fields at high current, and (viii) superposition of sputtering and evaporation for selected materials. The situation is even more complicated in reactive systems where the target surface chemistry is a function of the discharge conditions. While generally these factors imply a reduction of the normalized deposition rate, increased rates have been reported for certain conditions. Finally, some points of economics and “value added” are considered.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:20am **SE2-MoM10 Optical Diagnostics of HIPIMS Discharges: Dependence of Film Growth on Control Parameters**, ***M. Lange***, UTC and AFRL/RXBT, *J. Jones,* AFRL/RXBT, *C. Muratore,* UTC and AFRL/RXBT, *A. Reed,* AFRL/RXBT, *A. Waite,* UTC and AFRL/RXBT, *A. Voevodin*, AFRL/RXBT

High power impulse magnetron sputtering is a physical vapor deposition process distinguished by its capability to produce a high flux of ionized target material incident upon growing film surfaces. This characteristic gives the process advantages over conventional dc sputtering in that the orientation and relative density of thin films can be controlled by modulating the energy of ions constituting the film material. Unfortunately, the deposition rate in HIPIMS is often lower than in standard magnetron sputtering when processes conducted with the same time-averaged power are compared. The deposition rates for HIPIMS processes are dependent upon the power waveforms to the target, as well as the ionization energy, self sputtering rate, atomic mass, and other physical properties of the sputter target material. Correlation of target materials with thoughtfully selected properties to resultant plasma characteristics can reveal the nature of these relationships. For example, the ionization energies of hafnium and titanium are similar (6.8 eV), but their atomic masses of 178 amu and 48 amu respectively, affect the deposition rate in addition to the temporal-spatial plasma distributions, which were measured here using optical and electrostatic diagnostics. Studies of these materials provide insight on the effect of target mass on ion transport and film growth rates. Substrate bias and pulse duration have also been shown to effect the optical emissions from the plasma generated during HIPIMS operation. Correlation of these plasma characteristics to the structure and properties of elemental and compound thin films will be presented.

11:40am **SE2-MoM11 Time-resolved Plasma Characterization in Modulated Pulse Power (MPP) Magnetron Sputtering**, ***A.N. Cloud***, *R.E. Flauta, M.J. Neumann, S.L. Rohde, D.N. Ruzic*, University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HIPIMS/HPPMS) has attracted considerable attention from industry due its ability to produce thin films and features of excellent adhesion, superior density, decreased roughness, and extreme conformity. The intense pulsed plasma density – on the order of 10^{18} m^{-3} – provides a large concentration of metal ions that can be used to produce high-quality, homogeneous coatings. The high ionization fraction at the substrate allows for fine control of the sputtered species during deposition.

Modulated pulse power (MPP) can be employed to shape an arbitrary voltage waveform that is applied to the cathode. This programming freedom allows control over pulse duration, intensity, duty cycle, and average power. Voltage oscillations during the 1.0 – 3.0 ms pulse on the order of 25-65 kHz induce instabilities in the plasma discharge that may have a marked effect on the level of ionization within the discharge and distribution of the metal ions. The oscillation frequency range corresponds to the expected ion cyclotron angular frequencies. Past investigations of MPP have only revealed time-averaged plasma parameters, but knowledge of events during the pulse is required to further understanding of the physical mechanisms involved.

MPP discharges produced with a 1000 cm^2 circular planar magnetron were characterized. A gridded energy analyzer and quartz crystal microbalance were used to measure a higher ionization fraction than with conventional magnetron sputtering under a variety of deposition conditions. Nominal values of approximately 6% were attained for the sputtering of titanium at power densities as low as 100 W/cm^2. The energy spectrum and flux of these ions at the substrate location were also measured, finding the incident metal ions to be of low energy between 1 and 4 eV. Time-resolved plasma properties including saturation current, electron temperature, and density are measured and mapped over the three-dimensional space between the sputter target and substrate using a triple Langmuir probe. Plasma density is shown to decrease by greater than an order of magnitude between pulses. The effects of pulse duration, current density, pulse shape, switching frequency, and target material on the discharge are explored and discussed.

Plasma Science and Technology
Room: A1 - Session PS+MS-MoA

Plasma Challenges at the 22nm Node and Beyond
Moderator: C. Labelle, GLOBALFOUNDRIES

2:00pm **PS+MS-MoA1 Plasma Etch Challenges for 22nm Advanced Logic Development**, ***R. Wise***, IBM **INVITED**

At the 22nm technology node for logic devices many novel semiconductor technologies are being considered, each of which impacts etch process development and control. These technology performance challenges drive increases in carrier mobility (necessitating application of high strain liner and epi materials and reduction in silicon loss budget and gate height scaling), increased packing density (limiting resist trim budgets, increasing CD shrink requirements, and increasing integration of eDRAM), and achieving target resistance and capacitance (necessitating the introduction of porous low-k dielectrics and better profile control). The challenges introduced by these elements on dry etch processes, tooling, and controls is discussed in detail.

Widespread aggressive device scaling beyond lithographic limits require dry etch processes to provide controllable CD reduction to meet design groundrules. In particular, limited improvement in imaging at the 22nm node results in challenges in scaling on the plasma equipment. The implementation of multiple exposure techniques to achieve design rules for several key levels drives additional process control across multiple exposure and etch steps. Reduction in the available mask thickness required to preserve the lithography process window have driven the need for highly selective etch processes, generally at the expense of uniformity, defectivity, and profile of the transferred pattern. Later generation lithographic materials are expected to continue to exhibit increased sensitivity to line edge roughness, and drive additional implementation of novel masking materials. Process and tooling technology needs required to address these imaging challenges are discussed.

2:40pm **PS+MS-MoA3 22nm Technology Manufacturing Challenges - Window for Process Control becomes Smaller and Smaller, Equipment and Material Interaction Becomes Unpredictable and Manufacturing Costs Increase**, ***P. Adam***, GLOBALFOUNDRIES Dresden, Germany **INVITED**

Increasing complexity and smaller and smaller CD for 22 nm technologies will have also a major impact for all plasma supported processes. The limited understanding of plasma and device interaction in existing technologies will further challenge the equipment suppliers to develop solutions for high volume manufacturing fabs. Some examples will be shown to illustrate this statement. Fab Engineers will see unexpected behaviour of materials in process chambers and surprising results of their plasma process on the device itself. A big amount of this will not be seen in the application labs of the equipment suppliers. Part of the problem is availability of appropriate test wafer material which can reflect the final manufacturing situation sufficient enough. Designs from different companies will behave most likely also differently. Therefore equipment suppliers have to move their development process close into the manufacturing site of the fabs. On the other side, semiconductor fab would like to get a tool and a process ready to go. They don't have the time and the manpower to support this kind of development work for the equipment supplier. All this will drive additional cost for both supplier and costumer.

How we can overcome this situation? Some ideas will be presented highlighting the complexity of the situation and the need for close interaction of all involved parties.

3:40pm **PS+MS-MoA6 Logic Etch Challenges at the 22nm Node and Beyond**, ***V. Vahedi***, *G. Kamarthy, J. Guha, H. Singh*, Lam Research Corporation **INVITED**

Due to increased device integration complexity, there are significant challenges to technology scaling for Logic devices at 22nm and beyond. The issues range from difficulties in scaling device threshold voltage (V_t), and electron and ion mobility enhancements to achieving the proper leakage current for low power devices. Proposed solutions to overcome these challenges include adoption of Metal Gate High-k for threshold voltage and leakage current engineering, to various Strained Silicon techniques to enhance electron and ion mobility, and FinFETs for beyond 22nm technology node. In this presentation, we will review some of challenges associated with front-end logic integration schemes, such as control of Si Recess and Si damage. Si loss and damage after gate etch, spacer etch, and strained Si etch applications can impact source-drain junction depth, and increase device leakage. We will discuss various mechanisms for Si loss and damage, work done by previous authors, what is required at 22nm and beyond, implication for etch and post etch clean, and areas where better understanding is required.

Plasma Science and Technology
Room: A1 - Session PS1-TuM

Advanced FEOL and BEOL Etch
Moderator: Y. Kimura, LAM Research

8:00am **PS1-TuM1 Inductively-Coupled Pulsed Plasmas in the Presence of Synchronous Pulsed Substrate Bias for Advanced Gate Etching**, ***S. Banna***, Applied Materials Inc., *K. Tokashiki,* Samsung Elect. Co. Ltd., *A. Agarwal,* Applied Materials Inc., *J.Y. Lee,* Samsung Elect. Co. Ltd., *V. Todorow,* Applied Materials Inc., *J.H. Yoon,* Samsung Elect. Co. Ltd., *S. Rauf,* Applied Materials Inc., *K. Shin,* Samsung Elect. Co. Ltd., *K. Ramaswamy, P.J. Stout, D. Lymberopoulos, K. Collins*, Applied Materials Inc. **INVITED**

The pace at which microelectronics technology is progressing is highly challenging with conventional device architecture. The stringent and conflicting requirements in microelectronics for damage-free plasma etching processes, with improved uniformity, higher selectivity, better anisotropy, more precise ion energies/fluxes control and enhanced process throughput have stimulated an intensive research effort among academic and industrial communities. This research is focused on novel approaches for the design/control of the next generation of plasma processing reactors. Following the above challenges, the dry etch process regime for gate etching has moved towards low pressure plasmas with higher densities. In this regime, the risk of plasma induced damage(PID) or charging damage increases, potentially affecting the overall device electrical performance. PID includes UV damage and highly energetic ion bombardment damage. Moreover, for high aspect ratio structures, electron shading effect becomes more dominant enhancing the risk of charging damage. In the past, it was demonstrated that pulsed radio frequency(PRF) inductively coupled plasmas(ICP) have the promise to address some of the above challenges. Typical commercial ICP reactors consists of 2 RF power supplies, the RF source which is fed to the antenna coils of the ICP source and RF bias applied to the substrate. Accordingly, 3 main different regimes of operation for pulsed plasmas might take place. The first, known as source pulsing, in which the source is operating in PRF mode while having the bias in continuous wave(CW) mode. The second is bias pulsing i.e. source in CW mode while the bias is in PRF mode. The third one is synchronized pulsing, for which both source and bias are pulsed simultaneously at the same frequency and duty cycle.

Recently we have evaluated the impact of synchronized pulsing plasma on gate etch for sub-50nm DRAM applications. The evaluation included basic etching characteristics such as average etch rate, uniformity and selectivity, 35nm gate critical dimension(CD) uniformity and profile control, and plasma induced damage. It was demonstrated that by control of the synchronous pulse parameters extends the plasma operating conditions range aiming to improve processes for finer features. In particular, we have shown gate CD controllability, PID mitigation, and significant reduction in electron shading effect and in the gate leakage current along with improving the electrical performance of the overall device. 2D plasma and feature scale modeling results will be used to illustrate the basic physics of synchronous pulsing, in particular its effect on the ion energy distribution.

8:40am **PS1-TuM3 Synchronously Pulsed Capacitively Coupled Plasma Sources for Dielectric Etching**, ***A. Agarwal***, *P.J. Stout, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma etching processes for microelectronics fabrication at future technological nodes are extremely challenging. The requirements regarding the uniformity (both etch rate and critical dimensions) are also more stringent than ever. One particular challenge in plasma etching of extremely high aspect ratio features (aspect ratio > 40) is minimizing plasma induced damage, both physical and electrical. The via-like features may physically twist/turn due to the stochastic nature of fluxes entering the feature as the size of the opening shrinks.[1] Charge trapped by the polymer on the sidewalls exaggerates this phenomenon. Alternately, charge retention at the bottom of trenches may lead to breakdown as the material stresses under the accumulated charge creating a weak path for the injected current.[2] Pulsed plasma operation has been shown to be a promising approach to improving uniformity while reducing charge damage.[3] Although pulsing of both capacitively and inductively coupled plasma sources has been investigated before, novel pulsing schemes such as synchronous pulsing in multi-frequency capacitively coupled plasmas (CCP) may allow for expanded operating regime for damage-free etching of high aspect ratio features.

In this paper, pulsed and continuous plasma operation of a multiple frequency capacitive coupled plasma reactor in electronegative gas mixtures will be discussed using results from a computational investigation. A 2/3-dimensional plasma equipment model (CRTRS) [4] has been linked to a Monte Carlo feature profile model [5] to assess the consequences of pulsed plasma operation on etching of dielectric features. Results will be discussed for impact of pulse characteristics such as duty cycle, pulse excitation frequency, phase lag between source and bias pulses on dielectric etching in a multi-frequency CCP chamber. Careful tailoring of pulsing at both source and bias frequencies enables negative charge acceleration in the features and helps negate charge buildup. The impact of varying plasma electronegativity at different gas pressures will also be discussed. If strongly electronegative gas mixtures are used, sustaining a steady pulsed plasma can however be complicated as the plasma may not re-ignite after power is turned-off.

[1] A. Agarwal, M.M. Wang, and M.J. Kushner, 54th AVS Symposium 2007.

[2] T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696 (2008).

[3] S. Banna, et al., 55th AVS Symposium 2008.

[4] A. Agarwal, P.J. Stout, S. Rauf and K. Collins, 61st Gaseous Electronics Conference 2008.

[5] P. Stout, 60th Gaseous Electronics Conference 2007.

9:00am **PS1-TuM4 Highly Selective and Low Damage Etching of TiN / HfO_2 Layer Gate Stack Structure using Neutral Beam Etching and Atomic Layer Etching**, ***B.J. Park***, *J.B. Park, TH. Min, J.K. Yeon, S.K. Kang, W.S. Lim, G.Y. Yeom,* SungKyunKwan University, South Korea, *K.S. Min*, University of Texas, Austin

As the critical dimension of metal-oxide-semiconductor field-effect transistor shrinks less than 45 nm and below, conventional polysilicon gates on ultrathin SiO2 dielectric layers should be replaced by metal gates on high-k dielectric materials. However, the adoption of these new materials imposes new integration problems. Among many integration issues, the etch selectivity of the etched layers (metal electrode or high-k dielectrics) to the under-layers (high-k dielectrics or Si substrate) is one of the most important issues in the patterning of the gate stack structures.

In order to solve these problems, in this study, we applied two step etch process where, the metal gate electrode is selectively etched using a reactive neutral beam against a high-k dielectric layer and then the high-k dielectric layer is removed using atomic layer etching (ALET) for precise etch depth control.

The result showed nearly infinite etch selectivity of TiN/HfO2 using a HBr/Cl2 neutral beam by controlling energy (<100 eV). In addition, an anistropic etch profile and smooth surface roughness (0.109 nm) could be observed using TEM and AFM. For the ALET of HfO2, the monolayer etching condition of 1.2 Å /cycle could be observed using BCl3 ALET and, after the 30 etch cycles, exactly 3.5nm thick HfO2 layer was removed with a low surface roughness and without the change of surface composition. When we compared the properties of MOSFET devices fabricated using conventional RIE processing and those using the neutral beam/atomic layer etching, the improvement of characteristics of NMOSFET and PMOSFET could be observed for the devices fabricated using neutral beam /atomic layer etching.

ACKNOWLEDGMENT

This work supported by the National Program for Tera-Level Nano devices of the Korea Ministry of Education, Science and Technology (MEST) as a 21st Century Frontier Program.

9:20am **PS1-TuM5 Impact of Cure and Trim Processes on the Linewidth Roughness Transfer during Gate Stack Patterning with Amorphous Carbon Mask**, ***L. Azarnouche***, STMicroelectronics, France, *E. Pargon, M. Martin, O. Luere, K. Menguelti,* CNRS/LTM, France, *P. Gouraud, C. Verove,* STMicroelectronics, France, *O. Joubert*, CNRS/LTM, France

With the continuous scaling down of semiconductor device dimensions, the linewidth roughness (LWR) becomes a non negligible parameter that needs to be controlled in the nanometer range for the future technological nodes (1.7nm (3σ) for the 32 nm technological node). In previous studies, we demonstrated that the 193 nm photoresist mask LWR is the main contributor to the final gate LWR. We also observe that the LWR is mainly decreased during the plasma etching steps in which the resist mask is involved (BARC and hard mask etching). Preliminary conclusion is that the photoresist mask is the first vector of LWR decrease during plasma exposure. The resist LWR is therefore the key parameter to sucessfully control the final metal gate LWR in the nanometer range. In the present study, we first evaluate the impact of HBr cure plasma treatment and resist

trimming processes on the resist LWR and second analyze how these plasma etching steps impact the final gate LWR. LWR measurements are performed using the CD-AFM technique much more powerful than commonly used CD-SEM. First results indicate that both resist trimming and plasma cure treatment processes improve the resist LWR and consequently the final gate LWR. We demonstrate that, during cure processes, plasma Vacuum UltraViolet (VUV) light is mainly responsible for the resist LWR decrease while during trim processes, the plasma VUV light combined to the lateral erosion of the resist induced by reactive radicals is identified as the main contributor to the resist LWR decrease.

However, we also show that the sequence of cure and trim processes has a less important impact on the gate LWR than a cure or a trim process only and that the position of the cure treatment in the sequence of plasma etching steps involved in the gate patterning process has some consequences in the final gate LWR. Finally, as the etching mask used to pattern the gate plays a primordial role in the final gate LWR, we compare the impact of two masking strategies: one using amorphous carbon layer as etching mask and the other one a spin on carbon hard mask.

9:40am **PS1-TuM6 Multilayer Mask Etch - CD, CD Bias, and Profile Control using RLSA Plasma Etcher**, ***H. Kintaka***, *T. Mori*, TEL Technology Center, America, LLC USA, *M. Sasaki, 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), CD bias, and the mask profile control technique has been needed. As the result of this study, precise CD control of multilayer mask etching was established by RLSA (Radial Line Slot Antenna) microwave plasma source. The multilayer stack which was used for experiments consisted of Photo Resist/SiARC/Organic/SiN/Si-substrate.

The results are: first, zero Iso/Nest bias was accomplished. As result, the same CD bias is obtained kept in both the Iso and Nest pattern with vertical profile. Second, CD Bias is controlled in the range of several +/- nm with same bias of Iso/Nest by adjusting SiARC etching condition. By these characteristics, it is possible to make hard mask CD same as patterned resist CD in any pattern density.

These results are obtained by RLSA micro-wave plasma characteristics. RLSA generates high density plasma just below top dielectric plate, and as the plasma diffuses forward the wafer, its density and electron temperature become lower by diffusion. The etched by-products do not re-dissociate and not deposit on the wafer in the low electron temperature condition. This result shows that this plasma can etch only biased ion direction without side-wall deposition.

These unique characteristic will remove the burden of adjusting the width in the patterning step.

10:40am **PS1-TuM9 Effects of Hydrogen Bombardment during Polysilicon Gate Etching by HBr/O_2 Plasmas**, ***T. Ito***, *K. Karahashi*, Osaka University, Japan, *M. Fukasawa, S. Kobayashi, N. Kuboi, T. Tatsumi*, Sony Corporation, *S. Hamaguchi*, Osaka University, Japan

As the miniaturization of semiconductor devices continues, better control techniques of substrate surface damages as well as a better understanding of the mechanisms of surface modification during plasma processing are required for future semiconductor manufacturing. Especially during etching processes by HBr/O_2 plasmas, which are widely used for etching of poly-silicon gate electrodes, it has been reported that the silicon substrate under a gate oxide film is seriously damaged during the gate electrode etching process. This phenomenon is known as a “Si recess”. The goal of the present study is to understand the cause of the Si recess and to propose a technique to minimize it. To understand the mechanism, we have used a multi-beam injection system, which can irradiate surfaces with independently controlled atoms, molecules and ions. In this way, the system enables us to simulate experimentally plasma-surface interactions that take place during plasma etching processes. The multi-beam system consists of three parts, i.e., a mass analyzed ion beam injector, a set of two independently controllable neutral radical/molecular beam injectors, and a reaction chamber in which a sample substrate can be placed. In this system, a monochromatic and mono-energetic ion beam as well as independently controlled radical/molecular beams can be simultaneously injected into a given substrate surface. The ion and radical sources are differentially pumped and therefore the chamber can be maintained at ultra-high vacuum. The change in chemical nature of the substrate surface can be observed *in situ* by X-ray photoelectron spectroscopy (XPS) that is installed in the reaction chamber. In this study, Si(100) surfaces were irradiated by H^+, Ar^+, or O^+ ion beam at 500eV each as well as atomic oxygen (O) radical beams and are analyzed with (*ex situ*) High-Resolution Rutherford Backscattering (HRBS). The results have shown that a layer of structure alteration with 10 nm thickness is formed on the Si substrate surface only when H^+ ions are injected into the surface. Furthermore it has been found that oxygen (O) diffusion is enhanced in the alteration layer due to amorphization of Si. Thus our multi-beam injection experiments corroborates the hypothesis that the Si recess during HBr/O_2 plasma etching processes is caused by H^+ ion injections from HBr plasmas and O radical diffusion. This also suggests the importance of precise control of incident ion energies for the minimization of Si recesses during the processes.

11:00am **PS1-TuM10 Challenges in Etching sub-45nm Shallow Trench Isolation (STI)**, ***A. Paterson***, *T. Panagopoulos, S. Sriraman, A. Sato, N. Benjamin, N. Williams, C. Lee, Y. Yamaguchi-Adams, A. Eppler, L. Braly, T. Kim, H. Singh, V. Vahedi*, Lam Research

The continued scaling in semiconductor industry provides new challenges for etching Shallow Trench Isolation (STI) features to create active area islands. Control of the STI profile is of primary importance, e.g. trench angle control of 88° ± 0.2° being requested across a 300 mm wafer, along with the additional demand to control the trench depth range non-uniformity to <2.5%, for ~2500-3000 Å trench depth. Typically, the stringent profile control requirements are met by operating halogen based Transformer Coupled Plasma (TCP™) plasmas in the mid-pressure operating regime, 20mT to 60mT. However, in this regime the trench depth non-uniformity is upward of 5% and has a characteristic wafer pattern that resembles a “donut”, which is due to the electron mean free path, $\lambda_{mfp,}$ being short (e.g. 0.85cm for 20mT Cl2) compared to the chamber dimensions. The electrons and ions are predominately produced in the TCP’s torroidal power deposition region, with the torroid pattern then being transferred to the wafer plane through ion diffusion. The trench depth pattern can be substantially reduced by operating at lower pressure <5mT, such that the λ_{mfp} is comparable to the chamber dimensions and energized electrons can ionize neutrals with almost equal efficiency across the chamber, where the shape of the plasma density determined only by ambipolar diffusion. However, this severely inhibits profile control with trench angle and selectivity requirements not being met.

This paper will discuss the work undertaken at Lam Research to characterize halogen plasma’s produced by the TCP configuration of a Kiyo™ process chamber. Plasma diagnostic and simulation data shows that the plasma density uniformity can be substantially improved for a given pressure operation regime by optimizing the TCP hardware configuration. This optimization will translated into achieving <2.5% trench depth uniformity at mid pressure operation whilst maintaining profile control. Future challenges facing STI trench depth etch will also be discussed.

11:20am **PS1-TuM11 Control of TiN Sheet Resistance in Downstream Plasma PR Strip**, *V. Vaniapura*, ***L. Diao***, *S. Xu*, Mattson Technology, Inc.

Semiconductor integrated circuit density has increased continuously by shrinking the device size. Interconnects between multiple stacked metal layers need to be moved closer together hence thinner and narrower. However, the reduction of the interconnect dimensions increases electrical resistance and a subsequent loss of device performance. This leads to an ongoing effort to search for materials with lower electrical resistance suitable for interconnects to integrate into IC production. Metals like tungsten, titanium are good choices but require the use of conductive diffusion barriers. Titanium nitride (TiN) is widely employed as diffusion barrier layer and/or adhesion layer due to its low sheet resistance (Rs). Integration challenges occur with TiN during high temperature photoresist (PR) strip. The commonly used PR removal process, down stream oxygen plasma, can increase sheet resistance of TiN significantly. In order to understand how to reduce this adverse effect on the TiN layers, extensive studies of sheet resistance change (ΔRs) were conducted. TiN samples were treated with plasma exposure of different chemistries in an inductively coupled plasma reactor. Optical emission spectroscopy (OES) was used to observe the presence of reactive species in the plasma of different chemistries. The experimental results show that pure reducing chemistries were effective in maintaining the Rs, and the addition of these reducing chemistries to oxygen plasmas can significantly reduce ΔRs. OES analyses indicate that ΔRs is mainly caused by the oxidation of TiN with the present of reactive oxygen species in the plasma. Reactive oxygen content is controlled by the percentage of reducing chemistry in total flow. The dependences of ΔRs of TiN to various process parameters were investigated in detail. A majority of the Rs shift happens in the first tens of seconds of plasma exposure, which indicates that it is caused by modification of top surface. Based on this work, an optimized chemistry and process regime have been identified to greatly reduce or even suppress sheet resistance increase without compromising PR removal productivity.

11:40am **PS1-TuM12 Inductively Coupled Plasma Etching of GaN and Induced Defects**, ***J. Ladroue***, GREMI - STMicroelectronics, France, *A. Meritan, M. Boufnichel*, STMicroelectronics, France, *P. Lefaucheux, P. Ranson, R. Dussart*, GREMI, France

Wide bandgap materials such as gallium nitride are currently used for light emitter devices [1]. Otherwise, GaN physical properties open new prospects

in microelectronics manufacturing [2]. By combining a wide bandgap (3.4 eV), strong chemical bonds and high electronics mobility, GaN based devices should operate under higher temperature, higher power and higher frequency than typical silicon devices.

GaN etching is one of the first process steps in device structure developments. Due to inert chemical nature of GaN, wet etching is limited [3]. As a consequence, it is necessary to use dry etching method [4] to obtain a reliable MESA structures. Chlorine plasmas are commonly used because GaCl3 is the most volatile etching product. Due to the strong bond energy of III nitrides, GaN etching also requires high physical sputtering which is provided by heavy neutral gas like argon and high bias voltage.

In this study, the GaN etching was performed into an industrial Alcatel 601 E tool which consists of an Inductively Coupled Plasma source and a diffusion chamber [5]. This high density plasma system was initially dedicated to silicon deep etching and modified to use chlorine gases. Plasma is generated by a single-ring antenna coupled to a RF power supply operating at 13.56 MHz. The 6 inch chuck is independently biased and thermally regulated. The process gases including argon and chlorine (Cl2) are injected at the top of the source.

Cl2/Ar plasma etching was performed on GaN epitaxial layers (12µm) grown on sapphire by metalorganic chemical vapor deposition (MOCVD). After SiO2 deposition by Plasma Enhanced Chemical Vapor Deposition (PECVD), wafers were patterned using conventional photolithography. Samples were subsequently mounted on 6 inch coverplates made of different materials.

We have carried out a parameter screening to optimize the etch efficiency of GaN. The best results in term of profile quality are obtained with a silicon coverplate. An etch rate of 250 nm/min is reached with our current setup. However, defects like columns or pits are observed at the etched surface under some conditions. The origin of those defects is also investigated in this study. Moreover, diagnostics such as Langmuir probe, optical emission spectroscopy and mass spectrometry have been used to characterize the plasma and understand the etching mechanisms.

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Plasma Science and Technology
Room: B2 - Session PS2-TuM

Atmospheric Plasma Processing and Microplasmas
Moderator: Y. Sakiyama, UC Berkeley

8:00am **PS2-TuM1 Microplasma Synthesis of Dimensionally- and Compositionally-Controlled Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang, **R.M. Sankaran***, Case Western Reserve University

Microplasmas operated at atmospheric pressure in a continuous-flow geometry have tremendous potential for gas-phase nanoparticle synthesis. The non-thermal decomposition of vapor precursors in combination with the limited reaction volume afforded by microplasmas allows the fabrication of narrow dispersions of nanometer-sized particles (< 5 nm) *in a single step*. We have recently applied this technique to the synthesis of mono- and bimetallic nanoparticles for catalytic carbon nanotube (CNT) growth [1-3]. Dimensionally- and compositionally-controlled nanoparticles are initially prepared in a microplasma from metal-organic precursors such as ferrocene and nickelocene. To catalyze CNTs, acetylene and hydrogen gases are added to the particle flow exiting the microplasma reactor and heated in a tube furnace. Here, we show that the structure of as-grown CNTs is intimately related to the size and composition of the nanocatalysts. Reducing the mean diameter of the nanocatalysts to ~2 nm results in a high-purity of single-walled CNTs in the reactor product (>75 %). At a constant mean particle diameter, compositional tuning of bimetallic nanocatalysts is found to significantly alter the chirality distributions of the collected single-walled CNTs. In this talk, we will present the synthesis methodology, as well as detailed materials characterization of both the nanocatalysts and the CNTs.

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8:20am **PS2-TuM2 Argon-Methyldisiloxane-Oxygen Fed Atmospheric Pressure DBDs for SiO_2-like Thin Film Deposition**, ***F. Fanelli**, S. Lovascio, R. d'Agostino, F. Fracassi*, University of Bari, Italy

Organosilicon compounds, such as for instance hexamethyldisiloxane (HMDSO), mixed with oxidants (i.e. O_2 or N_2O) and noble gases (i.e. Ar, He), are widely used both in low pressure and atmospheric pressure plasma enhanced chemical vapour deposition (PE-CVD) of SiO_2-like coatings. In particular very recently atmospheric pressure dielectric barrier discharges (DBDs) fed with organosilicon monomers have been addressed as an attractive route towards the deposition of thin films. Since the deposition mechanism is not definitively known intense research efforts should be directed to the identification of the main reaction steps and to the correlation of the plasma chemistry with the coatings properties. For this reason in this work we report our recent results on the deposition of SiO_x thin films with atmospheric pressure DBDs fed by argon (Ar) in mixture with oxygen (O_2) and different methyldisiloxanes, i.e. hexamethyldisiloxane, pentamethyldisiloxane and tetramethyldisiloxane. The characterization of the deposited films was carried out by XPS, FTIR and SEM. The quali-quantitative determination of stable by-products contained in the exhaust gas, and formed by plasma activation, was performed by gas chromatography coupled with mass spectrometry (GC-MS). The influence of feed composition, in terms of chemical structure of the organosilicon compound and of the oxygen-to-monomer feed ratio, on the properties of the films as well as on monomer depletion and by-products concentration, was investigated.

Results show that in the absence of O_2 polymer-like coatings are deposited. Oxygen addition to the feed leads to a decrease of the carbon content of the film which is more evident when the number of methyl groups in the monomer is lower. GC-MS analyses allowed to appreciate that many linear and cyclic compounds, containing up to five silicon atoms, are formed in the plasma. As an example, in the case of HMDSO, the presence of species containing the dimethylsiloxane ($-Me_2SiO-$) repeating unit appears to be indicative of oligomerization processes (e.g. chain propagation, ring formation, and expansion reactions) which bring to linear and cyclic compounds with general formulas $Me-(Me_2SiO)_n-SiMe_3$ (n = 1-4) and $(Me_2SiO)_n$ (n = 3 - 4), respectively. The extent of unreacted monomer does not depend significantly on the feed composition even if the O_2-to-HMDSO feed ratio is varied in a wide range (i.e. 0-25). However, O_2 addition influences the quali-quantitative distribution of by-products.

The results allow to support hypotheses on the nature of films precursors as well as to clarify some aspects of the overall deposition mechanism and of plasma-surface interaction.

8:40am **PS2-TuM3 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition by Homogeneous Dielectric Barrier Discharge**, ***N. Gherardi**, L. Maechler, I. Enache, C. Sarra-Bournet, N. Naudé, H. Caquineau,* LAPLACE - CNRS - Université de Toulouse, France*, F. Massines*, Promes - CNRS, France **INVITED**

Low pressure plasma enhanced chemical vapor deposition (LP-PECVD) is widely used in the industry since it allows obtaining thin films without any substantial temperature increase. On the other hand, these last years, there has been an increasing interest in atmospheric pressure PECVD (AP-PECVD) since it can lead to an appreciable cost reduction. The potential cost saving is related to the suppression of the vacuum equipment and to the on-line processing capability.

In case of two dimensional materials such as rolls of thin polymer films, metal foils or glass plates, dielectric barrier discharge (DBD) appears as one of the most suitable discharges because it is a cold discharge, which is robust, and not disturbed by the motion of the substrate. DBDs normally operate in the usual filamentary mode, but it is now well-known that depending on the gas, electrical parameters, and electrode configuration, DBDs can also operate in homogeneous modes. Depending on the gas in which they are ignited, these homogeneous DBDs generally present different features. In the rare gases (helium, argon, neon…) they are known

as atmospheric pressure glow discharges (APGD) as they are characterized by high current densities and an electric field profile between the electrodes showing a cathode fall, a negative glow, a Faraday dark space, and a positive column. In nitrogen, they are called atmospheric pressure Townsend discharge (APTD) as they show lower current densities and a constant high field in between the electrodes.

If AP-PECVD can be achieved using filamentary discharges, the filamentary and statistical nature of this regime leads most of the time to a lack of control of the thin film quality, deposition rate and coating uniformity on large surface. Hence this paper focuses on an AP-PECVD process using homogeneous DBDs.

More precisely, we report here on the deposition of silicon based thin films using homogeneous DBDs working at atmospheric pressure, from hexamethyldisiloxane (HMDSO) diluted either in N_2 or in He, with or without small admixture of nitrous oxide (N_2O) as the oxidizing gas. Our approach consists in studying the thin film properties as a function of the discharge type (APGD or APTD) and N_2O content in the gas phase, using various surface analysis techniques: ellipsometry, profilometry, scanning electron microscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The gas phase is characterized mainly through optical emission spectroscopy. Results obtained either without motion of the substrate or in a roll-to-roll configuration are discussed, showing the capability of AP-PECVD to realize multilayers.

9:20am **PS2-TuM5 On the Deposition Mechanism of the Silica Like Films in Atmospheric Pressure Glow Discharge**, ***S.A. Starostin***, Eindhoven Univ. of Technology, The Nethelands, The Netherlands, *A.P. Premkumar,* Materials Innovation Institute (M2i), The Netherlands, *M. Creatore,* Eindhoven Univ. of Technology, The Netherlands, *H. de Vries, R.M.J. Paffen,* FUJIFILM Manufacturing Europe BV, The Netherlands, *M.C.M. van de Sanden*, Eindhoven Univ. of Technology, The Netherlands

Atmospheric pressure plasma enhanced thin film deposition (PECVD) is nowadays in focus of increasing scientific and industrial interest. The benefits of this newly emerging technology are in possibilities for cost-efficient in-line roll-to-roll production without expensive and cumbersome vacuum equipment. Yet, comparing to the well studied low pressure PECVD, there is a serious lack of insights on thin film deposition mechanisms on the moving substrates at high pressure.

In this contribution we present a study of the deposition process of silica-like films in the diffuse high power variety of the dielectric barrier discharge referred as atmospheric pressure glow discharge (APGD) [1, 2]. This process is capable to produce uniform carbon-free silica-like films on the polymeric webs in low cost gas mixtures [2]. Considering deposition mechanisms in a roll-to-roll atmospheric PECVD reactor with a moving polymer substrate and gas flow, three different pathways which are simultaneously contributing to the film formation can be identified: a) ionic deposition, where ionized products of the decomposed precursor drift in the electric field towards the surface; b) diffusive deposition of neutral radicals produced in plasma and afterglow phases and c) deposition of large particles or dust. Due to the gas flow and depletion of the precursor, each of these mechanisms leads to layers characterized by a specific composition, morphology and location within the discharge area. In this contribution we will address the influence of the different mechanisms on film deposition, supported by space-resolved spectroscopic ellipsometry, XPS, SEM and water contact angle measurements. The experimental profiles of the deposition rate along the gas flow were analyzed with a 2D numerical convection-diffusion deposition model.

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9:40am **PS2-TuM6 Industrial Scale Pulsed Atmospheric Dielectric Barrier Discharges**, ***B.D. Schultz***, *W.M. Hooke, W.F. Hargrove, A.R. Martin*, International Technology Center

Atmospheric dielectric barrier plasma glow-like discharges over 1 meter in length and 500 square centimeters in area have been generated in air with a custom high voltage driving source. Pulse peak currents well in excess of 1 kiloampere at atmospheric pressure with total charge transfer up to 90 microcoulombs have been repeatedly generated in homogeneous discharges at frequencies up to 100 hertz. A rapid voltage rise time at 20-30kV is readily achieved by the source and is sufficient to produce a voltage across the electrodes in excess of the DC breakdown voltage prior to the onset of breakdown. The overvoltage condition plays an important role in determining the uniformity of the plasma discharge. Electrical modeling of the discharge characteristics show the resistivity of the plasma to change over the course of an individual pulse causing the discharge characteristics to switch from an oscillatory state to a critically damped state. Charge transfer and power densities in dielectric barrier discharges are limited by the electrode size and the intrinsic material properties of the dielectric used to distribute the space charge. It will be shown that the charge transfer of each pulse scales proportionally with the size of the electrodes for a given dielectric as should be expected for a complete homogeneous discharge. This paper will emphasize the correlation between overvoltage conditions, dielectric material properties, and electrode size to the electrical charge transfer of the glow-like discharge. The impact of the charge transfer scaling behavior on the scaling of other critical parameters like current density will also be discussed.

10:40am **PS2-TuM9 Optical Emission Spectroscopy of an Argon DC Microdischarge: Electron Density and Gas Temperature Profiles**, ***S.G. Belostotskiy****, *T. Ouk, V.M. Donnelly, D.J. Economou,* University of Houston, *N. Sadeghi*, Université Joseph Fourier de Grenoble, France

Optical Emission Spectroscopy was employed to study a high pressure (100s of Torr) DC microdischarge in argon, with traces of N_2 and H_2 present and acting as optical tracers. Spatially resolved measurements of gas temperature across the 600 μm slot-type discharge were obtained from analysis of the rotational structure of two transitions of the first positive band of N_2: $B^3\Pi_g(v=4) \rightarrow A^3\Sigma_u^+(v=1)$ and $B^3\Pi_g(v=5) \rightarrow A^3\Sigma_u^+(v=2)$. Gas temperature profiles peaked at the cathode side of the discharge and slowly decreased towards the anode. Such behavior is consistent with the physics of DC discharges, where most of the power dissipation occurs in the cathode layer. The gas temperature increased with increasing current, reaching a maximum of T_g = 1200 K at I = 30 mA and P = 600 Torr. Electron densities were extracted from the spectral profile of the H_β line. The profile was fit with a Voigt function, which included Doppler, pressure, instrumental and Stark broadening. The electron density was estimated from the contribution of Stark broadening. The spatial profile of electron density was found to have a maximum in the cathode sheath edge region, followed by a minimum in the bulk plasma, and then a maximum some distance from the anode. This spatial distribution was explained by the non-homogeneous structure of the microdischarge, having a highly contracted positive column. The electron density near the sheath edge increased with both pressure and current reaching $n_e = 1.7\cdot10^{14}$ cm^{-3} at I = 30 mA and P = 600 Torr.

11:00am **PS2-TuM10 Argon Microplasma Diagnostics by Diode Laser Absorption**, ***N. Miura****, J. Xue, J. Hopwood*, Tufts University

Argon gas kinetic temperature and the resonance state ($1s_4$) density in argon microplasma were measured by tunable diode laser absorption[1]. The experimental argon gas pressure was varied from 1 to 760 torr. A 900 MHz microstrip split ring resonator[2,3] was used as the microplasma generator. A single-mode diode laser was tuned to scan through the argon 801.4nm line ($1s_4$-$2p_7$) by modulating the diode's driving current. The output of the diode laser was collimated and passed through the microplasma. The obtained absorption lineshapes were fit by a Voigt profile, which is the convolution of Gaussian and Lorentz profiles. The Gaussian part corresponds to Doppler broadening and the Lorentz part corresponds to collisional and Stark broadening. Under our high-pressure experimental conditions, collisional broadening dominates and Stark broadening are almost negligible. Since the Doppler and collisional broadening can be expressed by a single variable T (gas temperature), the absorption lineshapes were fit with two parameters, amplitude and gas temperature[4]. The line integrated density of the resonance state was estimated from the integral of the absorption profile. The line integrated densities of argon $1s_4$ are $1.7\text{x}10^{15}$ m^{-3} m at 1 torr and $1.4\text{x}10^{15}$ m^{-3} m at 760 torr with 1W of input power. The visually observed length of plasma decreases from 1 cm at 1 torr to a few hundred microns at 760 Torr. The measured gas temperature increases from 350 K at 1 Torr to 750 K at 760 Torr. The microplasma is also simulated using a fluid model, which is compared with experimental measurements.

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* PSTD Coburn-Winters Student Award Finalist

11:20am **PS2-TuM11 Experiment and Simulation Results of Limited Cathode Area MHCDs Operating in He**, ***R. Dussart,*** Universite d'Orleans - CNRS, France, *T. Dufour,* Universite d'Orleans, France, *L.J. Overzet, M. Mandra, J.B. Lee, M. Goeckner,* University of Texas, Dallas, *L.C. Pitchford,* CNRS - Laplace, France, *N. Sadeghi,* LSP - CNRS, France, *P. Lefaucheux,* CNRS, France, *P. Ranson*, Universite d'Orleans, France

Micro Hollow Cathode Discharges (MHCDs) offer the unique property to create DC micro plasmas in a stable regime at atmospheric pressure [1]. In collaboration with UTDallas (Texas), micro reactors are elaborated by usual microtechnology techniques (sputtering, electrodeposition, lithography, …), usually used in microelectronics and MEMS technology. A first set of microcavities in alumina were prepared and tested in helium. Optical and electrical characterizations were carried out in different cases: single or several cavity devices and for a limited or not cathode area. V- I characteristics were plotted in the different configurations and for different experimental conditions. When the cathode area is limited, an abnormal glow regime can be obtained, which favors the initiation of the plasma in multiple cavities [2]. By adding a small amount of N_2 to the discharge, the gas temperature was determined by fitting the second positive system $C^3Õ_u$-$B^3Õ_g$ emission spectra using the software developed at the LSP at Grenoble (France). Simulations of a single MHCD with variable cathode surface area were also carried out using the 2D code developed in Toulouse [3]. Simulation results will be compared to the experimental data. Finally, by applying voltage ramps to the microdischarge, hysteresis effects were observed and will be also discussed.

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11:40am **PS2-TuM12 Linear Microplasma Array using Strongly-Coupled Resonators**, ***J. Hopwood,*** *Z. Zhang*, Tufts University

Instabilities in atmospheric pressure plasmas are responsible for the irreversible glow-to-arc transition of cold microplasmas into destructive arcs. DC microplasmas are usually stabilized using a ballast resistor. Alternatively, AC microplasmas are controlled by rapidly extinguishing the discharge through the electrical charging of dielectric barriers surrounding the electrodes (*i.e.*, the DBD). The negative differential resistance of the glow-to-arc region also makes parallel operation of plasmas difficult. Stable arrays of DC and AC microplasmas, however, are possible using distributed ballasting[1]. In this work, we stabilize the individual microplasma using a quarter-wave resonator constructed from a microstrip transmission line. As the microwave input power increases, the microplasma's electrical resistance drops and the resonator is automatically quenched; thus arcing is avoided. Microwave impedance spectroscopy measures the plasma resistance as a function of input power and confirms the negative differential resistance of the microplasma. The technical challenge to operate multiple microwave resonators is met by employing coupled-mode theory[2]. An array of high-Q resonators will couple energy efficiently among themselves provided that all resonators share a common resonance frequency. A single microwave power source (400 MHz, 4 watts) drives the first resonator in a linear array and the remaining undriven resonators redistribute the input energy such that multiple microplasmas operate in a stable, parallel manner. Solutions to the classic coupled-mode theory equations are compared with electromagnetic simulations of the resonator array and with the observed excitation of multiple microplasmas. Having confirmed that coupled-mode theory is applicable to microplasma arrays, we then demonstrate the production of stable, high density ($n_e > 10^{14}$ cm^{-3}) cold atmospheric pressure plasma in a linear configuration that is suitable for high-rate material processing.

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Plasma Science and Technology
Room: A1 - Session PS-TuA

Fundamentals of Plasma-Surface Interactions I
Moderator: X. Hua, AMAT

2:00pm **PS-TuA1 Correlation between Surface Chemistry and Ion Energy Dependence of the Etch Yield in Multicomponent Oxides Etching**, ***P.-M. Bérubé***, *J.-S. Poirier, J. Margot, L. Stafford,* Université de Montréal, Canada, *P.F. Ndione, M. Chaker, R. Morandotti*, INRS-EMT, Canada

Progress in the development of advanced electronic and photonic devices strongly rely on the capability of etching multicomponent oxides such as $Ca_xBa_{(1-x)}Nb_2O_6$ (CBN), (Ba,Sr)TiO_3 (BST), and $SrTiO_3$ (STO) that exhibit ferroelectric and electro-optic properties of interest for these applications. An important issue in the development of plasma etching recipes for multicomponent oxides is that in contrast with simple, binary oxides such as SiO_2, ZrO_2 and HfO_2 the various atoms contained in the films are likely to interact differently with the various reactive species of the plasma. This makes investigations of the underlying physics and chemistry a very difficult task. In the present work, we propose a simple and effective way to examine the influence of surface chemistry on the plasma etching dynamics of multicomponent oxides. This method uses the energy dependence of the etch rate in combination with measurements of the total positive ion flux impinging onto the surface and relative positive ion composition of the plasma. Using pulsed-laser-deposited CBN and STO thin films as examples, it was found that the etching energy threshold, Eth, shifts towards values larger or smaller than the sputtering threshold depending on whether or not ion-assisted chemical etching is the dominant etching pathway. More specifically, displacement of Eth towards values larger than the sputtering threshold indicates an inhibiting surface chemistry while displacement towards lower energy is associated to an enhancing chemistry. For CBN films etched in an inductively coupled chlorine plasma, we measured Eth ~65 eV at 1 mTorr, ~240 eV at 10 mTorr, and ~400 eV at 15 mTorr. The threshold obtained in pure Ar plasma was similar to that achieved in Cl_2 at 1 mTorr, which suggests that CBN etching at low chlorine number densities is dominated by pure physical sputtering. This is consistent with TOF-SIMS measurements that showed comparable Ca, Ba, and Nb depth profiles for the samples etched in pure Ar and in 1 mTorr, Cl_2 plasmas. At 10 mTorr, the chlorine uptake was an order of magnitude higher than at 1 mTorr. In addition, we observed an important concentration of $BaCl_x$ and $NbCl_x$, with a considerable amount of non-volatile $BaCl_2$and $NbCl_2$ closer to the topmost surface. Therefore, the higher etching threshold observed at 10 and 15 mTorr results from the formation of reaction products that are more difficult to etch than the bare CBN surface. A similar inhibiting chemistry was observed for STO films etched in a fluorinated plasma. Eth increased from ~50 eV in pure Ar to ~90 eV in a 30%SF_6-70%Ar plasma, with the desorption of SrF_x compounds being the rate-limiting step.

2:20pm **PS-TuA2 Influence of Ion Energy and Ion Flux on Polystyrene Modification by Electron Beam Generated Plasma**, ***E.H. Lock****, S.G. Walton, R.F. Fernsler, M. Baraket*, Naval Research Laboratory

Electron beam generated plasmas constitute a unique class of plasmas due to their intrinsic low electron temperatures (< 1 eV), plasma potentials and thus ion kinetic energies. For the treatment of polymers, these plasmas have demonstrated the ability to change the surface energy and chemistry with limited change in surface topography and low etch rates. Successful increase in surface energy was achieved as a result of argon, oxygen and nitrogen treatments due to incorporation of oxygen and nitrogen functionalities. Treatment with SF_6 resulted in decrease of surface energy due to incorporation of fluorine groups. The surfaces were unchanged or even made smoother after argon and nitrogen treatments. Plasma generation in more aggressive media including oxygen and SF_6 resulted in surface roughness increase.

The dominant species driving the chemical modification process in electron beam generated plasmas differ from the ones observed in the conventional plasma sources because the high energy electron beam ionizes the gas much more efficiently and thus produces a significantly larger proportion of ions. Thus, the influence of metastables and photons is limited.

This study addresses the question of the influence of the increased kinetic energy and ion fluxes on the polymer surface modification. Ultra thin polystyrene film was chosen as a model substrate due to its well understood behavior. The changes in surface energy, chemistry, etch rates and glass transition temperatures of the polymer were investigated. The chosen gas environments are pure argon and argon/oxygen mixtures. Argon allows for studying the effects of surface activation and physical sputtering. In argon/oxygen mixtures the influence of reactive species is critical for the surface modification processes.This work was supported by the Office of Naval Research. E. H. Lock and M. Baraket appreciate the support of the National Research Council.

2:40pm **PS-TuA3 Energy Considerations in Plasma-Surface Interactions**, ***M. Goeckner****, C.T. Nelson, SP. Sant, E.A. Joseph, B.S. Zhou, L.J. Overzet*, University of Texas at Dallas **INVITED**

Plasma processes have been used for close to four decades in the semiconductor industry and even longer in other fields. Because such process systems are complex, many individuals subdivided the complete system into three main subsystems, gas-phase chemistry, plasma physics and surface chemistry/physics. Using this methodology, considerable knowledge has been gained in fundamental processes found in the gas-phase chemistry and plasma physics. Despite numerous high quality studies, understanding the surface subsystem has proven to be challenging. In part this is due to the interactions of the three subsystems. In this paper we will examine a model of plasma-surface interactions which is based on surface-averaged quantum mechanical processes. Using the model we arrive at a general model describing both etch and deposition. We will show how energy considerations, such a local surface temperature, play major roles in such processes. We will examine in some detail the link between the model and experimental data obtained from fluorocarbon plasmas. This work is supported by a generous gift from Applied Materials.

4:00pm **PS-TuA7 Effect of Energetic Ions on Plasma Damage of SiCOH Low-k Material**, ***E. Kunnen****, A. Urbanowicz, D. Shamiryan, H. Bender, A. Franquet, H. Struyf, W. Boullart, M.R. Baklanov*, IMEC, Belgium

In the semiconductor industry, the number of transistors per unit area has steadily increased over the past 40 years according to Moore 's Law. As a consequence, the distance between interconnecting copper lines has reached the dimensions where capacitive coupling between the lines becomes important. To reduce capacitive coupling, low-capacitive materials, so-called low-k materials, have been investigated and integrated. A lower capacitive value can be achieved by making hydrophobic porous materials from low polarizable molecules. However, during integration these materials are exposed to etch and strip plasmas, which results in a plasma damaged material with an increased k-value. In this study we want to shed light on the mechanism of how bombarding ions and chemically active radicals damage low-k materials.

As low-k, a SiOCH- based material was deposited on 300mm Si wafers, and porogen material was removed by UV curing, resulting in a 180 nm-thick layer with a porosity of 33%. Since the focus is on revealing the mechanisms and not limiting the damage, we use a pure oxygen plasma of which the damaging capabilities are well known. A transformer coupled plasma reactor, Lam Versys (r) 2300 (r), is used for exposure. This etch chamber allows a separated control of the power from the coil (top power or 'TP') on the one hand, and the power fed into the plasma through the wafer (bottom power or 'BP'). While TP results in dissociation of molecules, BP determines the bias voltage over which ions are accelerated to the wafer. Three conditions have been investigated: Bottom Power Only (BPO), Top Power Only (TPO) and Top Power and Bottom Power (T&BP), flow and pressure were kept constant. The photoresist etch rate for the different conditions was measured and the low-k wafers were exposed to the different plasma conditions using a normalized exposure time. The exposed layers were analyzed by Fourier Transformed Infrared Spectroscopy (FTIR), Water Contact Angle (WCA), Spectroscopic Ellipsometry (SE), Time Of Flight Secondary Ion Spectroscopy (TOFSIMS), Energy Filtered Transmission Electron Microscopy (EFTEM), Water and Toluene Based SE and mass measurements.

It was shown that the bombarding ions densify and seal the top layer, which makes it more difficult for the oxygen radicals to penetrate into the low-k and damage it. As a function of time, all applied conditions obey a logarithmic oxidation equation. A model that explains the equation is proposed: the oxygen radicals recombine to oxygen molecules in the damaged layer through surface reactions leading to an exponential decrease in radical concentration with depth resulting in the logarithmic time dependence.

4:20pm **PS-TuA8 193 nm Photoresist Roughening in Plasmas: VUV Photons and Synergistic Mechanisms**, ***M.J. Titus****, *D.G. Nest, D.B. Graves*, University of California, Berkeley

Plasmas can either roughen or smooth 193 nm photoresist (PR), but little is known about mechanisms or controlling variables. We report measurements of 193 nm PR roughness as a function of ion energy, substrate temperature, VUV fluence, and photon-to-ion flux ratio, in a well-diagnosed inductively coupled Ar plasma. Comparisons are made to analogous vacuum beam experiments. We seek to answer the question: what "knobs" control surface texture? We focus special attention on the role of VUV photons and their synergistic interactions with other plasma effects. Fourier transform infrared (FTIR) transmission measurements as a function of VUV photon fluence demonstrate that VUV-induced bond breaking occurs over a period of time. We present a model based on the idea that VUV photons initially deplete near-surface O-containing bonds, leading to deeper, subsequent penetration and more bond losses, until the remaining near-surface C - C bonds are able to absorb the incident radiation. Fitted model photo-absorption cross sections compare well with literature values. The model is tested and shown to be valid by comparing to measurements of VUV lamp exposures in a vacuum beam system and in the Ar ICP.

4:40pm **PS-TuA9 Electron, Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Roughening**, ***T.-Y. Chung***, *D.G. Nest, G.K. Choudhary, J.J. Végh, D.B. Graves,* University of California, Berkeley*, F. Weilnboeck, G.S. Oehrlein,* University of Maryland, College Park*, E.A. Hudson,* Lam Research Corp.*, M. Li, D. Wang*, Dow Electronic Materials

Previous vacuum beam studies showed that PMMA-based 193 nm photoresist (PR) will roughen due to the synergistic effects of ion bombardment, vacuum ultraviolet (VUV) photon flux and substrate heating [1]. FTIR measurements show that VUV photons break C-O bonds to a depth of about 100 nm in this PR. Using the same vacuum beam apparatus, we show that electron beam exposure (energies ~ 10^3 eV) of this PR results in similar C-O bond breaking. However, the effect of e-beams on PR roughening is very different from that of VUV photons. Electron beams can either promote or inhibit roughening with simultaneous ion and VUV photon exposure, depending on electron fluence. At high electron fluence, simultaneous e-beam/VUV/ion exposure appears to suppress VUV/ion-induced roughening. By contrast, lower fluence e-beams amplify the synergistic effects of ions and VUV photons, increasing roughness. It is known from electron beam resist studies that low fluence e-beams scission PMMA, but higher electron fluences induce cross-linking [2]. We tentatively conclude that any effect that amplifies PR scissioning during ion bombardment increases roughening, whereas any effect that induces cross-linking will suppress roughening. Finally, we discuss the nature of the dynamic changes occurring within the PR during separate and simultaneous exposures of ions, VUV photons and electrons.

[1] Nest, D., et al., Synergistic effects of vacuum ultraviolet radiation, ion bombardment, and heating in 193 nm photoresist roughening and degradation. *Applied Physics Letters*, 2008, 92(15).

[2] Hatzakis, M., Electron resists for microcircuit and mask production. *Journal of the Electrochemical Society*, 1969. 116(7): p. 1033.

5:00pm **PS-TuA10 Ion and VUV Radiation Induced Material Modifications of Advanced Photoresists During Plasma-Etching: Temporal Evolutions of Modified Surface Layers**, *F. Weilnboeck,* ***R.L. Bruce****, G.S. Oehrlein,* University of Maryland*, M. Li, D. Wang,* Dow Electronic Materials*, D.B. Graves, D.G. Nest, T.-Y. Chung,* University of California, Berkeley*, E.A. Hudson*, Lam Research Corp.

Plasma processes used for pattern transfer of nanometer structures can lead to severe material modification and roughness development of photoresist (PR) materials. We studied the temporal evolution of blanket and patterned films of fully formulated 193nm PR in Ar and Ar/C_4F_8 plasma discharges. The contribution of the optical radiation component to the overall material modification seen after direct plasma exposure was investigated by applying a filter approach which protects the PR against ion bombardment and neutral deposition. Different filter materials allow testing the influence of emission spectra and wavelength ranges of the plasma radiation from visible to vacuum ultraviolet (VUV) light. Material modifications were characterized by ellipsometry, x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, atomic force microscopy and scanning electron microscopy. In-situ ellipsometry, employing a setup which enables separation of the optical radiation component and other plasma components, enabled to investigate in real time PR degradation effects during plasma processing. The depth dependence of PR degradation was obtained by optical multilayer ellipsometric simulations of the data.

* PSTD Coburn-Winters Student Award Finalist

For the plasma discharge chemistries examined, the material modifications depended strongly on PR molecular structure, exposure radiation wavelength range and plasma chemistry. Material degradation was increased for increasing photon energy, and lead to substantial oxygen loss at the PR surface and in the PR bulk. The material modification depth showed a significant dependence on the emission spectrum of the plasma discharge. The amount of oxygen lost in the material bulk was found to directly correlate with a reduction in PR film thickness. Results indicate that compared to the pure Ar discharge (main emission at 104 and 106nm) material bulk modifications are significantly higher for Ar/C_4F_8 discharges (main emission above 130nm [1]) leading to PR film thickness reduction of up to 20nm. Whereas ion bombardment modified the PR to a depth of ~ 1nm for our conditions during the first few seconds of plasma exposure and then saturated, plasma radiation modified the PR near-surface region to a depth of several tens of nm over a period of tens of seconds.

[1] Woodworth, J.R., et al., Absolute intensities of the vacuum ultraviolet spectra in oxide etch

plasma processing discharges, JVST A, 2001, 19(1)

5:20pm **PS-TuA11 Mechanism for Generation of Molecular Level Line-Edge Roughness of ArF Photoresist during Plasma Etching Processes**, ***K. Koyama***, *B. Jinnai,* Tohoku University, Japan*, S. Maeda, K. Kato, A. Yasuda, H. Momose,* Mitsubishi Rayon Co., Ltd., Japan*, S. Samukawa*, Tohoku University, Japan

ArF photoresists, namely chemically amplified photoresists, have been used in recent 193-nm lithography processes. However, ArF photoresists have serious problems during plasma etching processes, such as line-edge roughness (LER). LER can be classified with pattern-size roughness, called "low-frequency LER," and molecular-level-size roughness, called "high-frequency LER". Especially, high-frequency LER is more serious problem for wiring in ULSI devices of less than 32 nm. In order to overcome these issues, it is essential to understand the relationship between irradiation species from plasma (ions, electrons, radicals, and ultraviolet/vacuum-ultraviolet (UV/VUV) photons) and molecular level reactions on the ArF photoresist surface.

In this study, we investigated the effects of UV/VUV radiation, ion bombardment and gas species on ArF photoresists by using our developed neutral-beam process. Samples were etched by Ar- or Cl_2-neutral beam and Ar- or Cl-ion and UV/VUV photon. The surface roughness of the films was measured by SPM. A comparison of neutral beam irradiation with ion and UV/VUV photon irradiation showed that surface roughness of ArF photoresist increased after ion and UV/VUV-photon irradiation for both gasses. Especially, in the case of chlorine gas, significant surface roughness is observed by adding UV/VUV photon. To investigate the effects of irradiation species on the ArF photoresist polymer structure, we analyzed the chemical bonding states in ArF photoresist polymers by using FTIR. FTIR measurement showed that the lactone and ester units in the base polymers were vulnerable to physical bombardment, chemical reactions, and UV/VUV photon irradiation. The vulnerability results in changes in base-polymer structure that could account for the differences in the etching rates and surface roughness of ArF photoresist films. Our results demonstrated that UV/VUV photon irradiation plays an important role for generation of molecular level line-edge roughness.

5:40pm **PS-TuA12 On the Absence of Post-Plasma Etch Surface and Line Edge Roughness in Vinylpyridine Resists**, ***R.L. Bruce****, *F. Weilnboeck, T. Lin, R.J. Phaneuf, G.S. Oehrlein,* University of Maryland*, W. Bell, C.G. Willson,* UT-Austin*, D.G. Nest, G.K. Choudhary, J.J. Végh, D.B. Graves,* UC-Berkeley*, A. Alizadeh*, GE Global Research

Reducing formation of line edge roughness during photoresist mask pattern transfer by plasma etching is becoming increasingly important as the critical dimensions of devices continue to shrink. We have found that using a nitrogen-containing polymer, poly(4-vinylpyridine) (P4VP), as resist completely eliminated plasma-induced surface and line edge roughening for pattern transfer process conditions that produced significant roughness in a wide variety of other polymers in Ar-containing gas discharges of various gas chemistries and over long plasma exposure times. This effect was investigated by considering the influence of the plasma species (ions, neutrals, VUV) as well as the polymer structure and comparing results with polymers that were prone to surface roughening, such as polystyrene. Material modification was characterized by in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy. Plasma-induced modifications in the polymer film are shown to cause changes in the mechanical properties at the surface leading to the development of residual stresses that creates surface roughness after plasma etching. We also investigated how nitrogen in the polymer structure as well as the gas discharge influences the mechanical stresses at the surface. Patterned films were also plasma-exposed to the same conditions and characterized by scanning electron microscope. The absence of surface roughness in P4VP is

shown to eliminate LER in 3D features. Finally, we provide a comprehensive model to show how the difference in the plasma surface modification in P4VP compared to polymers such as polystyrene leads to elimination of surface roughening.

Surface Science
Room: C1 - Session SS1+PS+TF+AS+NS-TuA

Non-Thermal Chemistry / Ion, Electron Processes
Moderator: A.V. Walker, University of Texas at Dallas

2:00pm **SS1+PS+TF+AS+NS-TuA1 Growth and Purification of Nanostructures Deposited by Electron Beam Irradiation: A Surface Science Perspective**, ***H. Fairbrother***, *J. Wnuk, J. Gorham, S. Rosenberg,* Johns Hopkins University*, T. Madey,* Rutgers*, W.F. van Dorp, K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam induced processing (FEBIP) of volatile organometallic precursors has emerged as an effective and versatile method of fabricating metal-containing nanostructures. However, to improve the materials properties of FEBIP nanostructures, provide information that can aid in the rational design of new precursors and improve the modeling of the FEBIP process it is necessary to better understand the molecular level processes associated with the electron stimulated decomposition of organometallic precursors. To address this issue, we have employed a UHV-surface science approach to study the electron induced reactions of dimethyl(acetylacetonate) gold(III) ($Au(acac)Me_2$), a common precursor used for Au deposition in FEBIP, adsorbed on solid substrates. Surface reactions, reaction kinetics and gas phase products were studied using incident electrons in the energy regime between 40-1500 eV, using a combination of XPS, RAIRS and MS. XPS data indicate that electron irradiation of $Au^{III}(acac)Me_2$ is accompanied by the reduction of Au^{III} to a metallic Au^0 species embedded in a carbon matrix while MS reveals the concomitant evolution of methane, ethane and hydrogen. The electron stimulated decomposition of the $Au^{III}(acac)Me_2$ precursor can be described by a first-order decay process with respect to the surface coverage, with a rate constant that is proportional to the electron flux and a total reaction cross-section of $\approx 3.6 \times 10^{-16}$ cm^2 at an incident electron energy of 520 eV. As a function of the incident electron energy, the maximum deposition yield was observed at ≈175 eV. Our results are consistent with the idea that those carbon atoms removed as volatile species from the $Au^{III}(acac)Me_2$ precursor during FEBIP are associated with methyl groups attached to the central Au atom. In related studies we also studied the effects of atomic oxygen and atomic hydrogen on Au-containing carbonaceous films deposited by electron beam irradiation of $Au(acac)Me_2$, as a potential route to purify FEBIP deposits. Atomic oxygen was found to be the more effective of the two radical treatments in removing carbon, although a surface layer of gold oxide was formed. Subsequent exposure of this overlayer to atomic hydrogen rapidly removed the oxide, resulting in a pure Au film. AFM analysis of FEBIP deposits before and after radical treatment support the idea that carbon abatement is accompanied by a decrease in particle size.

2:20pm **SS1+PS+TF+AS+NS-TuA2 Surface Morphology Control and 3D Structure Development with Cryogenic Assisted Electron Beam-Induced-Deposition**, ***M. Bresin,*** *K.A. Dunn*, University at Albany SUNY

Electron beam-induced-deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID. 3D structures were developed using a multilayer deposition method, facilitating the creation of hanging, suspended or incorporated-gap structures.

Experiments were performed using an FEI Nova 600 Nanolab dual beam system with a LN2 cryogenic stage, enabling substrate temperatures of -155±5oC. A gaseous platinum precursor (MeCpPtMe3) was first condensed onto the cooled substrate using a capillary-style gas injection system (GIS). Condensate thicknesses between 100nm-3mm were produced by adjusting the GIS-substrate gap and precursor crucible temperature. Next, gas flow was terminated and the condensate was irradiated with an electron beam to induce precursor decomposition. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions showed clear evidence of successful deposition. The morphology of the deposited material depended on exact deposition conditions, and exhibited several distinct types absent from deposits made by conventional (room temperature) EBID.

3D structures were developed with a multilayer deposition method. In this method, multiple layers were used to take advantage of the electron penetration depth within the condensate, through which the depth of deposition could be controlled. An initial layer was first condensed and a region was deposited with the electron beam to act as a substrate-anchoring site. A second condensed layer was then applied such that electrons could only penetrate to the top of the initial condensed layer. The electron beam was then shifted, to deposit a section partially over the anchoring region (in the initial layer) with the remainder over unreacted area. After reheating, part of the second deposit was found to have adhered to the anchoring region, while the rest hung over vacuum. Using similar process, structures were also developed to create embedded gaps or tunnels.

Taken together, these observations have important implications for the creation of arbitrarily large or complex structures previously untenable by EBID fabrication. The growth mechanism and potential applications will be discussed, from nanotechnology to osteointegration.

2:40pm **SS1+PS+TF+AS+NS-TuA3 Nanoscale Patterning and Graphene Film Deposition on Si using Low-energy Electron Beams**, ***T.M. Orlando***, *D. Sokolov, D. Oh, K. Shepperd*, Georgia Institute of Technology **INVITED**

The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for many electron-beam induced processes in materials growth, etching, and lithography. We have demonstrated experimentally and theoretically that the total ESD yield of adsorbates can be a function of the incident low-energy electron-beam direction. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). We have also explored three graphene growth strategies which utilize low-energy electron beams and non-thermal reactions. The first uses electron beam irradiation in conjunction with chemical vapor deposition techniques to grow graphene directly on Si substrates. This approach utilizes unsaturated hydrocarbon precursor molecules and can be carried out at relatively low temperatures. The second involves electron-stimulated removal of oxygen and organic fragments from graphene-oxide flakes positioned on patterned Si substrates. This may allow for damage-free reduction of graphene-oxide to graphene. The third involves electron-beam removal of defects from graphene expitaxially grown from SiC(0001) substrates.

4:00pm **SS1+PS+TF+AS+NS-TuA7 A Study of the Nucleation of Focused Electron Beam Induced Deposits: Growth Behavior on the Nanometer Scale**, ***W.F. van Dorp***, Delft University of Technology, The Netherlands*, J.B. Wagner, T.W. Hansen, R.E. Dunin-Borkowski,* Danish Technical University, Denmark*, K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam-induced deposition (FEBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled nearly to the level of single molecules. Currently, the highest resolution that is reported is 0.7 nm [1] using the precursor $W(CO)_6$. At this scale, deposits contain no more than a few molecules on average. Our ultimate goal is to develop the ability to deposit single precursor molecules in a consistent manner.

We perform our FEBID experiments in environmental scanning transmission electron microscopes (E-STEM) with a beam energy of 200 keV and a 0.2 nm probe. The annular dark field (ADF) signal is used for the imaging of the deposits. By recording the ADF signal during deposit growth we are able to monitor the growth process in situ. Thin, electron transparent graphite is used as a substrate and typical precursor gas pressures at the sample during the deposition were 10^{-3} to 10^{-5} Torr.

In the present study we used $Me_3PtMeCp$, a Pt-precursor that is often used in FEBID experiments [2]. To improve on the currently achieved resolution, it is important to study the nucleation stage of deposits. When using a graphite substrate we found that there is a significance difference in deposition behavior between the $W(CO)_6$ and $Me_3PtMeCp$ precursors. Where the typical growth behavior for $W(CO)_6$ is to form nm-sized or even sub-nm sized deposits, the deposits fabricated from $Me_3PtMeCp$ are a few nanometers in diameter and consist of individual sub-nm sized grains. We report on our study of this difference in growth behavior and strategies to increase the writing resolution.

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruit, Nanotechnology 19 (2008) 225305

[2] A. Botman, M. Hesselberth, J.J.L. Mulders, Microelectron Eng 85 (2008) 1139

4:20pm **SS1+PS+TF+AS+NS-TuA8 Direct Local Deposition of High-Purity Pt Nanostructures by Combining EBID and ALD**, ***A.J.M. Mackus***, Eindhoven University of Technology, the Netherlands, *H.J.J.L. Mulders, A.F. de Jong,* FEI Electron Optics, the Netherlands, *M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions electron beam induced deposition (EBID) has the potential to become a key nanomanufacturing technology. The technique suffers however from incomplete decomposition of the precursor gas and consequently a low material purity. Platinum EBID yields typically only a purity of ~15 at.% and a resistivity value orders of magnitude higher than bulk resistivity which reduces the functionality of the material for most nanoprototyping applications such as adding electrical contacts to nanodevices. In this contribution we propose a novel approach for the fabrication of high-purity Pt nanostructures based on a combination of the patterning capability of EBID and the high material quality obtained by atomic layer deposition (ALD). The latter technique yields submonolayer control of the film thickness and in the case of Pt ALD high purity (~100%), low resistivity (13±1 μΩcm) films [1]. The developed approach comprises seed layer deposition by EBID and area-selective ALD growth. For specific conditions the thermal ALD process of Pt ($MeCpPtMe_3$ precursor, O_2 gas) was found to start selectively on an EBID seed layer with a thickness equivalent to one monolayer Pt. It was established that the deposits have a uniform thickness and a high purity value (>93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. In addition to the approach and the material properties the underlying reaction mechanism of the (area-selective) Pt ALD process will be discussed, including aspects such as the role of dissociative chemisorption of O_2 molecules on Pt and the formation of H_2O, CO_2, and CH_4, reaction products.

[1] H.C.M. Knoops, A.J.M. Mackus, M.E. Donders, M.C.M. van de Sanden, P.H.L. Notten, and W.M.M. Kessels, *Electrochem. Solid-Sate Lett.* **12**, G34 (2009)

4:40pm **SS1+PS+TF+AS+NS-TuA9 Anionic Surface Processes Induced by Low-Energy Electrons**, ***P.A. Rowntree***, University of Guelph, Canada **INVITED**

The historical development of surface chemistry has largely been based on the use of free-energy-driven processes; an enormous volume of literature exists that details the search for chemical control over these processes using the classical parameters of temperature, surface composition and reagents. However, as the interest in controlling the processes grows, and the need to produce structurally resolved reactive systems increases, alternative non-thermal mechanisms are increasingly being explored in order to drive the interfacial processes into reaction channels chosen by the needs of the operator instead of the principles of thermochemistry. Our specific interest is in the control of surface processes using low-energy electrons as specialty 'reagents' that can be delivered to surfaces in a highly controlled manner, and interact with surface species according to understandable and reproducible mechanisms. The overall goal is to understand and manipulate these mechanisms to selectively interact with target molecules of our choosing to modify surfaces according to our needs.

This presentation will focus on two aspects of this 'manipulative' approach to surface chemistry. The first is our recent development of ways to selectively control where incident electrons interact with the organic monolayers that are deposited on Au(111) surfaces. These chemically homogeneous monolayers have a highly uniform electronic structure along the length of the chains, such that it is normally not possible to strongly enhance the dissociation probabilities at any given site. We have found that it is possible to selectively enhance the rupture of C-H bonds at the methyl terminations of these films by coupling the incident electron flux with anionic excitonic states of rare gas solids that are adsorbed on these methyl terminations. The energy+charge transfer process that leads to bond rupture is extremely sensitive to the incident energy as well as the chemical nature of the target species, thus enhancing the selectivity of the local modifications to the organic surface. A second set of processes will be discussed that involves the electron-induced decarbonylation of metal carbonyls adsorbed on organic surfaces to produce atomic metal deposits. We have shown that low-energy electrons can induce surface polymerization reactions in $Fe(CO)_5$ films that lead to apparent CO-elimination cross-sections greater than 1 nm^2. This strong coupling to dissociative processes allows us to develop thin metal overlayers without the substrate damage that is usually associated with using thermal evaporation or sputtering processes.

5:20pm **SS1+PS+TF+AS+NS-TuA11 Condensed Phase Electron-Stimulated Reactions: Desorbed Anions and Retained Radicals**, ***Y. Shyur***, *J. Wang, S. Lau, E. Krupczak, C. Arumainayagam*, Wellesley College

Studies of low-energy electron-induced processes in nanoscale thin films serve to elucidate the pivotal role that low-energy electron-induced reactions play in high-energy radiation-induced chemical reactions in condensed matter. While electron-stimulated desorption (ESD) experiments conducted <u>during</u> irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products <u>following</u> low-energy electron irradiation can provide new insights into radiation chemistry. We have used post-irradiation temperature-programmed desorption to identify labile radiolysis products as demonstrated by the first identification of methoxymethanol as a reaction product of methanol (CH_3OH) radiolysis. Although low-energy electron-induced oligomerization reactions have been previously reported for molecules such as thiophene and cyclopropane, our electon-induced studies of CCl_4 represent the first study to specifically identify the products of such reactions, demonstrating the utility of post–irradiation temperature programmed desorption experiments to study the radiation chemistry of condensed matter. Results of post-irradiation studies have been used not only to determine the identity of radiolysis products, but also to determine the dynamics of electron-induced reactions. By comparing our post-irradiation results to previous electron stimulated desorption studies of anion production during irradiation of condensed CF_2Cl_2 and CF_3I, we examine the relationship between desorbed anions and retained radicals during dissociative electron attachment in the condensed phase.

5:40pm **SS1+PS+TF+AS+NS-TuA12 Cluster-induced Desorption and Ionization of Biomolecules for Application in Mass Spectrometry**, ***M. Dürr***, Hochschule Esslingen, Germany, *C. Gebhardt, A. Tomsic, H. Schröder, K. Kompa*, MPI für Quantenoptik, Germany

Mass spectrometry of biological macromolecules has developed into a key technology for fast routine analysis in biotechnology. A critical issue is the efficient transfer of non-volatile biomolecules out of their sample solution into the gas phase in combination with their concomitant ionization. Here we show that a beam of neutral molecular clusters consisting of 10^3 to 10^4 SO_2 molecules can be used for the desorption and ionization of biomolecules. Cluster impact on arbitrary surfaces pre-treated with biomolecules efficiently creates cold, desolvated, gas phase biomolecular ions as large as 6000 u without any need for preparation of the biomolecules in a special matrix or post-ionization after desorption. Since the cluster provides not only the energy for the desorption process but also a transient matrix during the process, the molecules are found to be desorbed without any fragmentation.

As revealed by means of molecular dynamics simulations, high kinetic temperatures in the order of a few thousand Kelvin are reached during cluster impact on the surface. However, these extreme conditions prevail only for some picoseconds, since shattering of the initial cluster leads to very fast energy dissipation. Already after 20 ps, the SO_2 cluster fragments have reached a temperature colder than the original temperature of the adsorbates. This fast energy dissipation excludes efficient energy transfer into the vibrational degrees of freedom relevant for the cleavage of the relatively large biomolecules and thus allows for their soft, fragmentation-free desorption.

Plasma Science and Technology
Room: Hall 3 - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Extension of Aluminum Etch using a Carbon Mask for High Aspect Ratio 70nm Al Etch with a Chlorine Based Chemistry, ***G. Ding***, *B. Schwarz, C. Lee*, Applied Materials, Inc

A strippable amorphous carbon hardmask has many advantages over traditional resist or oxide hard masks, it is widely used in frond end applications. However carbon masks for Al etch in backend applications has not been employed. The final CD as well as the aspect ratio that can be achieved with a carbon based mask for Al etching, and how that mask would benefit over traditional PR masks and oxide hard mask are discussed. In this study, we focused on non-fluorine or low-fluorine containing chemistries to achieve a high mean wafers between clean (MWBC) performance. The selectivity/budge for the film stacks (PR => SiON => carbon film =>Al etching) using this approach are illustrated. The carbon mask has shown to achieve less than half of final CD while doubling the mask selectivity over than those best achieved in the PR mask. CD uniformity of **5** nm (3sigma) uniformity was achieved. We demonstrate a wide range of CD tunability (± 20 nm). Throughput and throughput optimization is discussed. The different passivation mechanisms for different masks, PR mask, Oxide hard mask and carbon mask in Al etch are discussed. We demonstrated similar trends between resist and carbon and baseline what leads to excellent transferability of the etch process. This study shows the significant process benefit of the carbon-Al etch in comparison to the oxide HM and PR mask, which will allow Aluminum etch to be continued from an etch perspective to sub 50nm lines with 6:1 aspect ratio.

PS-TuP2 A Study on the Etching Characteristics of Magnetic Tunnel Junction Films for Spin Transfer Torque MRAM, ***M.S. Lee***, KAIST, Republic of Korea, *J.Y. Moon, S.H. Cho, J.K. Jung, S.K. Lee, H.S. Kim, S.K. Park*, Hynix Semicon., Republic of Korea, *W.J. Lee*, KAIST, Republic of Korea

As one of the candidates for universal memory, spin transfer torque MRAM (STT-MRAM) based on magnetic tunnel junction (MTJ) shows several important features such as nonvolatility in data storage and fast writing speed (2~4ns). The most critical engineering challenge for the fabrication of STT-MRAM is the development of etching technology. The etching of magnetic films has severe problems due to the nonvolatility of the metallic byproducts at practical processing temperature. The chlorides, fluorides, bromides and iodides of transition metals have much higher boiling temperatures compared to those of the typical materials used in semiconductor industry. In addition to this intrinsic problem, we should make the MTJ etching profile more vertical while minimizing the redeposition in order to avoid electrical shorting between free layer and pined layer in MTJ structure.

The object of this study is to provide characteristics of dry etching process available for sub 100nm STT-MRAM application. In this study, we investigate the effect of noncorrosive gas chemistry on MTJ etch rate, profile angle and hard mask selectivity, as a function of various process parameters such as RF power, working pressure, gas flow rate and ESC temperature in ICP etching system. It is also examined how the post etching treatment including oxygen plasma ashing and wet cleaning process affects the interface of MTJ films. The characteristics of MTJ interface are carefully analyzed by using high resolution transmission electron microscope (HR-TEM), electron energy-loss spectroscopy in the TEM (TEM-EELS) and X-ray photoelectron spectroscopy (XPS). Highly anisotropic profile of nearly 80 degrees is obtained by optimizing the etching condition and hard mask process scheme. Electromagnetic characteristics are also reported as a function of various etching conditions.

PS-TuP3 Interactions of Plasma with Dielectrics during Ultra Low-k Dual Damascene Etch, ***Y. Zhou***, *R. Patz, A. Darlak, K. Zhou, J. Pender*, Applied Materials, Inc., *C. Labelle*, GLOBALFOUNDRIES, *D. Horak*, IBM Research

Higher porosity and new film chemistries are required to drive down the k value of porous ultra low k dielectrics integrated in advanced BEOL stacks. In the k=2.2 porous SiCOH films used in 32nm and 22nm BEOL stacks, higher carbon content and higher Si-C/Si-O ratio render these films more chemically similar to photoresist and to SiCN barrier layers. Hence, there is greatly reduced selectivity between the mask and low-k dielectric, and between the low-k dielectric and the barrier film. The via etch process has to move to a drastically different plasma regime in order to achieve mask selectivity and barrier selectivity, as well as to control RIE lag. New film chemistry and increased porosity also result in new film/plasma interactions, such as surface roughness phenomena 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 modification point. In this work, film surface roughness phenomena will be examined for a k=2.2 porous SiCOH film utilizing a via first trench last integration scheme. Experiments show that surface roughness can arise from several etch steps if plasma conditions are not carefully controlled. Results will be presented with some of the process regimes explored.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

PS-TuP4 Highly Selective Etching of Silicon Nitride to CVD a-C in Dual-Frequency Capacitively Coupled CH_2F_2/H_2 Plasmas, *J.S. Kim*, ***N.-E. Lee***, Sungkyunkwan University, Korea

For the fabrication of a multilevel resist (MLR) based on amorphous carbon (a-C) layer and Si_3N_4 hard-mask layer (underlayer), etch selectivity of the Si_3N_4/a-C layer becomes increasingly critical with the feature size reduction. In this work, therefore, the highly selective etching process of the Si_3N_4 layer using chemical-vapor-deposited (CVD) a-C etch-mask was investigated by varying the following process parameters in $CH_2F_2/H_2/Ar$ plasmas: etch gas flow ratio, high-frequency source power (P_{HF}) and low-frequency source power (P_{LF}) in a dual-frequency superimposed capacitively coupled plasma etcher. It was found that infinitely high etch selectivities of the Si_3N_4 layers to the CVD a-C on both the blanket and patterned wafers could be obtained for certain process conditions. In particular, the etch gas flow ratio was found to play a critical role in determining the process window for infinite Si_3N_4/CVD a-C etch selectivity, due to the change in the degree of polymerization. The etch results of patterned ArF PR/BARC(bottom anti-reflective coating)/SiO_x/CVD a-C/Si_3N_4 MLR structure supported the possibility of using a infinitely high selective etch processes of the Si_3N_4 layer using a very thin CVD a-C etch-mask for reduced overall aspect ratio of MLR structure during patterning.

PS-TuP5 Infinitely High Selective Etching of ITO Binary Mask Structure for Extreme Ultraviolet Lithography (EUVL), *Y.R. Park*, ***N.-E. Lee***, Sungkyunkwan University, Korea

Currently, extreme ultraviolet lithography (EUVL) is being investigated for next generation lithography. Among the core extreme ultraviolet lithography (EUVL) technologies, mask fabrication for EUVL is of considerable importance due to the use of new reflective optics having a completely different configuration compared to those of conventional photolithography. This study investigated the etching properties of EUVL binary mask structure including newly proposed absorber layer of ITO, Ru (capping/etch-stop layer), and Mo-Si multilayer (reflective layer) by varying the gas flow ratio, dc self-bias voltage (V_{dc}) and etch time in Cl_2/Ar inductively coupled plasmas. ITO absorber layer needs to be etched with no loss of Ru layer on the Mo-Si multilayer for fabrication of the EUVL ITO binary mask structure proposed here. The ITO layer could be etched with an infinitely high etch selectivity over Ru etch-stop layer in Cl_2/Ar plasmas with V_{dc} of -50 V even with increasing over etch time. Etching of the stacked mask structures with a 200-nm line/space e-beam resist pattern showed a vertical profile and an etch-stop on the Ru etch-stop layer.

PS-TuP6 Improvement of Surface Roughness in SOI Wafer Fabrication using Cl_2-based Neutral Beam Etching, ***TH. Min***, *J.K. Yeon, B.J. Park, S.K. Kang, W.S. Lim, G.Y. Yeom*, Sungkyunkwan University, Korea

For the next generation silicon substrates applied to nano-scale semiconductor devices, silicon-on-insulator (SOI) wafer is known to be one of the outstanding candidates because of the advantages such as high speed, high packing density, immunity from latch-up, low power dissipation, high resistance to ionizing radiation, etc.

For the SOI wafer, the surface roughness of SOI wafer is very important because it can change the physical and chemical properties of the top silicon layer of the SOI wafer. Many approaches have been attempted to reduce the surface roughness of the SOI wafer by chemical mechanical polishing, high temperature annealing, wet etching, etc. but these methods are known to have some problems such as long processing time, reliability of exact thickness control, etc.

In this study SOI wafers were etched by a chlorine neutral beam obtained by the low angle forward reflection of an ion beam and the surface roughness of the etched wafers was compared with that of the SOI wafers

etched by a chlorine ion beam. The result showed that the surface roughness of the SOI wafer etched by the chlorine neutral beam was significantly improved compared to that etched by the chlorine ion beam. By etching about 150nm silicon of about 300nm-thick top silicon layer of SOI wafer using the chlorine neutral beam, the rms surface roughness lower than 1.5 Å could be obtained with the etch rate of about 750 Å /min while that etched by the chlorine ion beam showed the rms surface roughness higher than 2.5 Å.

The induced defects in the surface area of the SOI wafer by the ion beam and neutral beam were observed by high-resolution-transmission-electron-microscopy(HR-TEM). An atomic force microscopy(AFM) was employed to measure and evaluated the surface roughness of the SOI wafer before and after the etching process, respectively.

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PS-TuP7 *In-situ* Evaluation of Ashing Plasma Damages on Porous SiOCH Films Due to Ions, Radicals, and Radiation, ***H. Yamamoto***, *K. Takeda, M. Sekine, M. Hori,* Nagoya University, Japan, *T. Kaminatsui, K. Yamamoto, H. Hayashi, I. Sakai, T. Ohiwa*, Toshiba Corporation Semiconductor Company, Japan

Low dielectric constant (low-*k*) materials for interlayer dielectric are important for the improvement of ULSI devices performance. 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. The *in-situ* evaluation is crucial for the clarification of damage generation mechanism because the damaged low-*k* films are modified after exposing to atmosphere. This work investigated the mechanism of plasma ashing damage on the porous SiOCH films by *in-situ* evaluation. We examined the effect of ions, radicals, and radiation using PAPE technique. The thickness and refractive index of porous SiOCH films were measured using *in-situ* spectroscopic ellipsometry. Si-CH_3 bond absorption was measured using *in-situ* FT-IR.

The ashing plasma was exited in a 100 MHz CCP etcher. We adopted porous SiOCH films (k = 2.3) as low-*k* films in this study. The ashing process condition was total gas pressure of 2.0 Pa, 100 MHz source power of 450 W, substrate temperature of 20 °C. In the evaluation, a Si plate or a MgF_2 window which transmits the radiation (greater than 115 nm in wavelength) were placed at 1 mm above or just on the low-*k* film during the ashing. We carried out 4 kinds of experiments : (a) nothing for evaluating of the interaction of ions, radicals, and radiation, (b) Si plate for evaluating of the effect of radicals, (c) MgF_2 window for the interaction of VUV radiation with radicals, (d) MgF_2 window with no space for the effect of VUV radiation.

In the case of H_2 plasma ashing, we confirmed that the interaction of ions, radicals, and radiation or that of radicals and radiation decreased the thickness of the porous SiOCH film. The interaction of radicals and radiation caused the increase of the refractive index. The interaction of ions, radicals, and radiation or that of radicals and radiation caused the decrease of Si-CH_3 bond absorption.

The experimental results showed that H radicals extracted Si-CH_3 bond and that effect was drastically promoted by radiation and ions. The decrease of Si-CH_3 bond caused the decrease of polarizability and density of the film. However, ions made the film contract. Then, the refractive index of the films exposed to ions, radicals and radiation drastically increased. From these results, we proposed a mechanism of the plasma damages on porous SiOCH films.

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PS-TuP9 Origin of Electrical Changes Occurring at Plasma Etching Endpoints, ***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 impedance magnitude, phase, and dc self-bias voltage. Consequently, these electrical signals are useful for endpoint detection, i.e., for determining when to stop an etch. However, the mechanisms responsible for the observed electrical changes are not well understood. To investigate these mechanisms, we performed experiments and numerical modeling of CF4/Ar plasma etches of thermal silicon dioxide films on silicon substrates, in an rf-biased, inductively coupled plasma reactor. A wave cutoff probe was used to measure the plasma electron density as a function of time during etching. As the etch breaks through the oxide and exposes the underlying silicon, changes in the gas-phase densities of etch products and reactants cause the electron density to increase. This increase (and an accompanying increase in ion current) has a large effect on the measured electrical signals. Using a numerical model and measurements made at varying bias frequencies, the effect of changes in electron density can be distinguished from smaller effects caused by other parameters that may vary at endpoint, including the electron temperature, average ion mass, and the ion-induced emission of electrons from the wafer surface. In addition to explaining the experimental results, the model provides predictions, over a wide range of conditions, for the sensitivity and reliability of the electrical endpoint signals.

PS-TuP10 Optimization of Precursor Injection in an Atmospheric Pressure Plasma Jet System, ***F.J.J. Peeters***, Eindhoven University of Technology, The Netherlands, *R. Dams, R. Rego, M. Dubreuil, D. Vangeneugden,* Flemish Institute for Technological Research (VITO), Belgium, *M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition (AP PECVD) of thin films is a recently emerged technology, showing important advantages in comparison with the traditional and well established low pressure plasma enhanced deposition methods. The main benefit of AP-PECVD is the potential of cost efficient in-line production without expensive and bulky vacuum equipment.

In this work, an innovative AP plasma jet system is investigated which serves as a pilot system for industrial scale equipment, the VITO PlasmaLine®. Applications include moisture/oxygen diffusion barriers as well as grease barriers, UV curing of coatings or chemical activation of a surface. For industrial application a high throughput (~ 100-1000 m/min) is critical in order to compete with conventional techniques, such as wet chemical coating. Barrier coating deposition by AP-PECVD on polymer substrates has been demonstrated to be superior to wet chemical coating, with less consumption of precursor material [1], though many technical challenges remain to obtain the desired (dynamic) growth rates.

The pilot equipment utilizes a 0.5 mm double slit configuration with 1000-2000 W power input at a frequency of 40-50 kHz with N_2 as the primary carrier gas. By utilizing the plasma afterglow remote from the source, uniform surface treatment can be achieved despite the filamentary discharge in the slits. Deposition on the electrodes is prevented by injection of precursor into the jet and because of the remote nature of the plasma source the thermal load on the substrate is minimized, making it ideally suited for treatment of polymers and paper.

A key area for improvement and upscaling of the pilot system for industrial application is optimization of gaseous and liquid (aerosol) precursor injection. To this end, extensive characterization of the plasma jet is undertaken, including current-voltage, fast imaging and optical emission and absorption measurements, with focus on the dynamics of gaseous and aerosol precursor particles in the jet. For optimum control over the gas distribution and precursor injection, Computational Fluid Dynamic models are presented in conjunction with the experimental work.

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PS-TuP11 Plasma Etching of SiO_2 Using a Pin-To-Plate Dielectric Barrier Discharge in Atmospheric Pressure, ***J.S. Oh***, *J.B. Park, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

These days, atmospheric pressure plasmas are being investigated as the application to the flat panel display device processing such as indium tin oxide etching, the deposition and etching of thin film transistor materials (SiO_2, amorphous silicon, and Si_3N_4) in addition to the surface treatment. Especially, among the various atmospheric pressure plasmas sources, much attention has been paid to Dielectric Barrier Discharge (DBD) due to its potential to numerous industrial applications such as plasma ashing, etching, thin film deposition, etc. The DBD, which is consisted of two parallel electrodes covered by dielectric plates, has been studied most widely due to the easier generation of stable glow discharges and the possibility of large-area plasma processing compared with other atmospheric pressure plasma sources.

In this study, using a modified DBD called "pin-to-plate DBD", SiO_2 was etched and its plasma characteristics were investigated. Especially, the effect of additive gas such as CF_4 and C_4F_8 gas to the gas mixture of N_2 (60 slm)/ NF_3 (600 sccm) on the SiO_2 etch characteristics was investigated. The results showed that the increase of C_4F_8 (200 ~ 800 sccm) to the gas mixture decreased the SiO_2 etch rate continuously, while, the addition and increase of CF_4 (1 ~ 10 slm) to the gas mixture increased the SiO_2 etch rate until 7 slm of CF_4 was added and the further increase of CF_4 decreased the SiO_2 etch rate . The increase of SiO_2 etch rate up to 7 slm CF_4 is from the effective removal of Si in SiO_2 by F atom through the removal of oxygen in SiO_2 by carbon in CF_X in the plasma. However, the decrease of SiO_2 etch

rate with further increase of CF_4 was related to the formation of a thick C-F polymer layer formed on the SiO_2 surface. The SiO_2 etch rate of about 243 nm/min could be obtained with the gas mixture of N_2 (60 slm)/ NF_3 (600 sccm)/ CF_4 (7 slm) when input voltage and operating frequency to the source were 10 kV and 30 kHz, respectively.

PS-TuP12 Diagnostic Study of Microplasmas in Contact with Saline Solution, *H.W. Chang, **A.H. Hsieh**, C.L. Chen, C.C. Hsu*, National Taiwan University, Taiwan

Microplasmas in contact with saline solution are studied. This microplasma is sustained using a DC power source with the output voltage up to 600 V and the current up to 1.5 A. The powered electrode is the electrode at which the plasma forms. It consists of a thin platinum wire (0.5 mm in diameter) covered by a glass tube except the 2-mm near-tip area. The grounding electrode is a 1 cm * 3 cm- and 0.5-mm-thick stainless steel sheet plate. Both electrodes are immersed in saline solution of various concentrations. The powered electrode serves either as the anode or the cathode, depending upon the operating condition chosen. Diagnostic tools used in this work include a voltage probe and a current probe to monitor the voltage and the current waveforms at the electrode, respectively; an optical emission spectrometer was used to monitor the time-averaged emission spectra. It is shown that the microplasma in 1 M saline solution can be ignited without difficulty for the voltages above 300 V. The forming and sustaining of the microplasma have been found to be a complicated phenomenon associated with the bubble formation and the plasma ignition in the bubbles. As the powered electrode is positively powered (i.e. the anode), two discharge modes, high and low current modes, have been identified. In the low current mode, the microplasma appears to be more stable, and the bubble stays and attaches at the tip of the powered electrode steadily for many seconds, while in the high current mode, the bubbles continuously forms and detaches from the electrode. The major optical emission lines in the high current mode are Na (589 nm) and H (656 nm) emissions. In this presentation, the potential use of this microplasma for materials processing will be discussed.

PS-TuP13 Synthesis of Niobium Oxide Nanowires Using an Atmospheric Pressure Plasma Jet, ***Y. Lin**, C.C. Hsu*, National Taiwan University, Taiwan

The fabrication of niobium oxide nanowires using an atmospheric pressure plasma was performed. An arc plasma jet sustained by a pulsed power supply with the repetitive power frequency of 25 kHz was used. The O_2 plasma jet was used to treat the 0.025 mm-thick unannealed niobium foils to fabricate niobium oxide nanowires. It was found in this work that the distance between the foil and the jet appears to be the most critical operating parameter for nanowire fabrication. Niobium oxide nanowires with different morphologies were fabricated with oxygen plasma jets at an applied voltage of 300 V and a flow rate of 45 slm, with the foil located at 0.3 ~ 0.7 cm downstream of the plasma jet. Depending upon the distance between the foil and the jet, as well as the operating conditions, the nanowire diameter ranges from 100 to 500 nm, with the length being up to 6 µm. Current work shows that the nanowire diameter increases over time under plasma treatment. Energy-dispersive spectroscopy reveals that the stoichiometry of the fabricated nanowires have the composition ranges from NbO to NbO_3, depending upon the conditions. In this presentation, the correlation between the plasma characteristics and the nanowire structure and its composition will be discussed.

PS-TuP14 Study of an Atmospheric Pressure, Pulsed Arc Plasma Jet: Downstream Characterization and its Application to Thin Film Deposition, ***Y.W. Hsu**, Y.J. Yang, C.C. Hsu*, National Taiwan University, Taiwan

An arc plasma jet operated under atmospheric pressure was studied. This plasma jet is able to generate a stable plasma using a DC pulsed power source of 20 kHz ~ 40 kHz using nitrogen, oxygen, and clean dry air. In this presentation, diagnostic studies of the plasma jet downstream and the use of this jet for metal oxide fabrication will be presented. The plasma jet downstream was characterized using multiple diagnostic tools. The electrochemical sensor was used to quantify the downstream NO/NO_2 concentration. Multiple thermocouples were used to directly measure the jet temperature and the optical emission of the jet was monitored by an optical emission spectrometer. Spatial-resolved measurements were performed using the above-mentioned diagnostic tools. The downstream species measurements show that the NO density increased from 5 to 116 ppm and the NO_2 decreased from 93 to 52 ppm at 5 cm downstream of the nitrogen plasma jet when the applied voltage increased from 150 V to 350 V under a constant gas flow rate of 45 slm. Jet downstream temperature measurements show that at 1.5 cm downstream of the jet the temperature is approximately 100 °C with 250 V applied voltage and 45 slm. This plasma jet was used for ZnO thin-film deposition. Different precursor injection systems, including a bubbler and an ultrasonic atomizer, were tested. It is shown that the ZnO thin film can be deposited on the glass substrate as confirmed by X-ray photoelectron spectroscopy. The deposition rate and the film quality can be optimized by varying the operating parameters. The correlation between the plasma characteristics and deposited thin film properties will be discussed.

PS-TuP15 Amorphous Silicon Etching Using Atmospheric-Pressure Dielectric Barrier Discharge (APDBD) Plasma, ***H.C. Kwon**, G.H. Kim,* Seoul National University, Korea*, S.H. Lee,* Korea Institute of Materials Science, Korea*, T.H. Noh,* National Fusion Research Institute, Korea*, S.I. Choi, S.G. Kim, S.K. Lim*, Samsung Electronics Co. Ltd, Korea

Since the process area has been enlarged for increasing the fabrication rate of TFT-LCD, the atmospheric process has been attractively considered. Among the atmospheric processes, the etching is the most challengeable due to the difficulty of etch pattern control and charge damage. Here the etch properties of atmospheric-pressure dielectric barrier discharge (APDBD) has been investigated for the system size of 300 mm × 80 mm. The etching process has been accomplished at 2~3 mm below a blower type APDBD which is a closed system consisted of the top and bottom dielectric electrodes to generate the DBD plasma. Thus, the introduced etchants (SF_6) with carrier gas (N_2) are discharged in the DBD source chamber and the radicals are extruded through the hole of DBD source into the target of amorphous silicon (a-Si) on the patterned silicon nitride (SiNx) with photoresist (PR). The target is set on the moving stage with maximum speed of 100 mm/s. Thus the charge damage may not be considered in this etching system. The etch profiles were exampled with AFM, SEM and others. Result shows the availability of a few micron patterns and etch rate of 600 Å/min with the uniformity below 10% over the substrate. The etch rate and uniformity are sensitive to gas flow rate, the gas mixing ratio, the substrate temperature and the substrate motion. The electrical and optical methods were employed to monitor the discharge properties as the plasma density and gas temperature in source chamber, respectively. Tentatively, it concluded that the ATM process has the property in between the wet and dry (vacuum) process due to its highly collisional condition. The radical generation and transport in the system play a key role in improve the etching, which will be presented.

PS-TuP16 Poly(ethylene glycol) Films Deposited by Atmospheric Pressure Plasma Liquid Deposition and Atmospheric Pressure Plasma-Enhanced Chemical Vapour Deposition : Synthesis of Non-Fouling Surfaces, ***B. Nisol***, Université Libre de Bruxelles, Belgium*, C. Poleunis, P. Bertrand,* Université Catholique de Louvain, Belgium*, F. Reniers*, Université Libre de Bruxelles, Belgium

The role of protein-repelling coatings is to limit the interaction between a device and its physiological environment, by inhibiting the non-specific protein attachment. Plasma-polymerized-PEG (*pp*-PEG) surfaces are of great interest since they are known to avoid protein adsorption [1]. In this study, *pp*-PEG films have been deposited on gold and polyvinylfluoride (PVF) surfaces, by means of atmospheric pressure plasma liquid deposition (APPLD) and atmospheric pressure plasma enhanced chemical vapour deposition (APPECVD) processes. A comparison between those two methods has been made by investigating the chemical composition of the films using infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS) and secondary ions mass spectroscopy (SIMS). By observing the C1s high resolution XPS spectra of our samples, it appears that for APPECVD samples, the hydrocarbon component (285 eV) is increasing as the power of the plasma is increased, revealing a higher fragmentation of the precursor (tetra(ethylene glycol)dimethylether), while for APPLD samples no changes occur. The same conclusion could be made by observing the typical ToF-SIMS peaks (m/z = 45 (CH_3-O-CH_2^+ and $^+CH_2CH_2$-OH), 59 (CH_3-O-CH_2-CH_2^+), 103 (CH_3-(O-CH_2-$CH_2)_2^+$)) that are decreasing in the case of high powered APPECVD treatments. The non-fouling properties of our samples have been studied with Bovine Serum Albumin (BSA) adsorption. On that purpose, XPS was used to track the presence of BSA on the surface by using the N1s signal coming out from the protein. For the APPECVD samples, a low plasma power (30 W) leads to an important reduction of BSA adsorption (over 90% reduction). However, higher-powered treatments tend to reduce the non-fouling ability of the surfaces (around 50% of protein adsorption reduction for a 80 W deposition). The same order of magnitude of BSA adsorption reduction (over 90%) is obtained for the APPLD surfaces, whatever is the power of the treatment. Those results show an important difference between APPECVD and APPLD processes in terms of power of the plasma treatment.

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PS-TuP17 High Refractive Index Polymeric Optical Coatings by Plasma Polymerization, ***L.D. Hyde****, H.J. Griesser*, Ian Wark Research Institute, Australia

The technique of plasma polymerization has attracted much interest for its ability to deposit uniform polymeric coatings whose thickness can be controlled with nanometer precision via the plasma duration. Thus, plasma polymer (PP) films are well suited to application in optical precision instruments and other devices where high quality optical films are required. However, the range of refractive indices (RI) reported for plasma polymers is quite narrow. One objective of our research is to study how higher RI values can be achieved. Another objective is to develop PP coatings whose RI varies gradually, from a value matching the substrate to a higher value. Gradient Refractive Index (GRIN) films have been produced by plasma polymerization, with the RI changing linearly with the film composition [1]. Here we report on the plasma polymerization of bromoethane and other brominated monomers to create a database of RI versus PP composition prior to using such data for producing GRIN PP films. Factors affecting the PP film composition and thus the RI are plasma deposition power, pressure, deposition rate, and the monomers themselves. Characterization of compositionally homogeneous PP films is performed by optical techniques such as ellipsometry and the data obtained can be extrapolated to provide information about graded polymer films. This is also the case when analyzing homogenous polymer films with techniques such as x-ray photoelectron spectroscopy and Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). However, several complementary techniques must be employed when analyzing GRIN films. Techniques such as Small Angle X-ray Scattering (SAXS) and X-ray Reflectometry (XRR) have been utilized because the power of x-rays allows the RI in any medium to be assumed to be unity, as opposed to other optical techniques that essentially deal with optical interfaces and assume samples to be optically homogenous. SAXS is particularly useful as it is capable of measuring polymer blends. Similarly, neutron techniques such as neutron reflectometry (NR) and Small Angle Neutron Scattering (SANS) are complementary to x-ray techniques, as shown by previous work where PP films were analyzed using both XRR and NR [2]. Studies are currently underway to examine the composition of homogenous PP films. One interesting method for depth profiling thin polymer films is TOF-SIMS analysis with a C_{60} gun, which has been used to characterize discrete multilayer structures [3].

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PS-TuP18 HfSiON Growth from Hf Metal/SiO_2/Si(100) Stack with Nitrogen VHF-ICP Exposure, ***R. Kage****, T. Kitajima, T. Nakano,* National Defense Academy, Japan*, T. Makabe*, Keio University, Japan

In the paper, we show the new fablication scheme of high-k dielectric thin film for MOSFETs with fewer process steps, lower impurity, and minimised EOT (equivalent oxide thickness). In the process, high density hafnium metal nano particle with 4 nm diameter is formed on SiO_2/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with SiN interfacial layer.

Current ULSI technology requires the use of hafnium related high-k dielectrics with ~3 nm thick for MOSFET to lower

the power consumption. HfSiON is the most applicable chemistry for the high-k material with proper energy band

alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO_2 utilizing the thermal interfacial reaction was previously proposed [1]. The process demonstrates remarkably low inpurity in the film due to the lack of carbon in contrast to the case of MOCVD processes. In our case, 2.5 nm thick Hf metal layer is deposited with e-beam deposition source on SiO_2/Si(100) surface uniformly. The

morphology obtained with the in-situ non-contact AFM measurement revealed the surface consists of the high density array of Hf nano particles with the size of 4 nm in diameter.

The exposure of atomic nitrogen and ions from the non-equiliblium plasma enables the introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are

oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS

analysis. The following plasma exposure (~10min.) enables the diffusion of Si atoms into the higk-k film from the

underlying SiO layer. The Si content in the film increases with the exposure time and becomes comparable to the Hf content with 35 min. exposure. The XPS spectrum shows the Si incorporated is mostly nitrided in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

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PS-TuP19 Plasma Characterization of an Unbalanced Magnetron Sputter Deposition System, ***K. Pollock****, J. Hiltrop, J. Doyle*, Macalester College

We present a study of the near substrate plasma properties in an unbalanced magnetron deposition system used to deposit hydrogenated amorphous germanium thin films. The system is equipped with external Helmholtz coils that allow control over the near substrate plasma density. Four plasma diagnostic methods are used to characterize the plasma; a cylindrical Langmuir probe, a flat probe with a guard ring, a retarding field analyzer, and optical emission spectroscopy. The complementary nature of the diagnostics results in a robust determination of the plasma density, electron temperature, and plasma potential. The plasma density inferred from the cylindrical and flat probe results are corroborated by the relative ion currents to the retarding field analyzer. The latter also allows determination of the plasma potential, which agrees well with that inferred from the cylindrical probe results. The electron temperature inferred from the cylindrical probe is approximately corroborated by the relative intensity of the argon optical emission lines, but there is also some evidence that the electron energy distributions have a non-Maxwellian part. In our system the near substrate plasma density can be varied by about a factor of 25. Higher plasma densities near the substrate result in a lower electron temperature and a slight negative shift in the plasma potential. Hydrogen-argon mixtures results in large increases in both plasma density and electron temperature compared to argon-only plasmas. Possible reasons for this phenomena are discussed.

PS-TuP20 Deposition Profile of Carbon Films in Submicron Wide Trenches using H-assisted Plasma CVD, ***T. Nomura****, J. Umetsu, Y. Korenaga, H. Matsuzaki,* Kyushu University, Japan*, K. Koga, M. Shiratani,* Kyushu University, and JST, CREST, Japan*, Y. Setsuhara,* Osaka University, and JST, CREST, Japan*, M. Sekine, M. Hori*, Nagoya University, and JST, CREST, Japan

In recent years hard carbon films have attracted much attention due to their high hardness and wear resistance.[1] Deposition profile of hard carbon films in trenches is one of the concerns. We have succeeded in controlling deposition profile of Cu in trenches of 100 nm in width, and have realized sub-conformal, conformal and anisotropic deposition profiles using H-assisted plasma CVD.[2-4] Here we report these three deposition profiles of carbon films obtained using the H-assisted plasma CVD. Experiments were performed using the H-assisted plasma CVD reactor, in which a capacitively-coupled 28 MHz main discharge and an inductive-coupled 13.56 MHz discharge for an H atom source were sustained.[2-4] This reactor provided independent control of dissociation of deposition material and generation of H atoms. Toluene diluted with H_2 and Ar was supplied at flow rates of 80sccm and 10sccm, respectively. The total pressure was 13 Pa. First, we have studied dependence of deposition rates at the bottom and sidewall of trenches on discharge power of the H atom source. The deposition rates tend to decrease with increasing the power, probably because the flux of H atoms, which etch carbon films, on the surfaces increases. Next, we have studied dependence of the deposition rates on kinetic energy of ions impinging on the surfcases. The deposition rate at the bottom increases significantly with increasing the kinetic energy of ions, while that at the sidewall does not. Irradiation of high energy ions modifies carbon films into a hard structure and the etching rate of such hard carbon films is considerably reduced.[1,5] Another important parameter for deposition profile control is identified to be the substrate temperature. By tuning the H atom flux, ion energy, and substrate temperature, we have realized sub-conformal, conformal and anisotropic deposition profiles of carbon films. Film qualities such as atomic compositions, structure will be presented at the conference.

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PS-TuP21 Carbon Particle Formation Due to Interaction between Graphite and Helicon Plasmas, ***M. Shiratani****, S. Iwashita, H. Miyata, K. Koga*, Kyushu University, Japan

Formation of dust particles due to plasma-surface interaction has attracted a great deal of attention in many fields because dust particles can cause

quality deterioration in semiconductor manufacturing [1, 2] and can contain a large amount of tritium in fusion devices [3], and so on. Therefore, it is important to reveal their formation mechanisms, their transport as well as their accumulation area. Up to now, we have collected carbon dust particles formed due to interaction between graphite target and helicon plasmas using in-situ and ex-situ collection methods [4], and have analyzed them. Here we report experimental results regarding carbon particle formation due to interaction between graphite and helicon plasmas and discuss their formation mechanisms.

Experiments were carried out with a helicon plasma reactor. Hydrogen or deuterium plasmas were generated by applying pulsed rf voltage of 13.56 MHz to a helicon antenna. The ion density and electron temperature obtained in the helicon discharge reactor are $4x10^{10}$-$3x10^{12}$ cm^{-3} and 4.5-11.8 eV, respectively. Dust particles collected in the helicon plasma reactor can be classified into small spherical particles, agglomerates whose primary particles are around 10 nm in size and large irregular particles. There are many small dust particles of 1 nm-1 μm in size. The typical density ratio among them is $2x10^3$: 1: 3. The smaller their size is, the higher their number density is. The size regions of these dust particles are 1-500 nm for small spherical particles, 50-700 nm for agglomerates and 50 nm-6 μm for large irregular particles, respectively. The three kinds of dust particles suggest three formation mechanisms: CVD growth, agglomeration, and peeling from walls. The dust particles of 10 nm in size have the highest probability to be charged positively, whereas those above 30 nm in size are charged negatively [5]. Agglomeration between a negative large agglomerate and a positive small dust particle takes place during the discharging period.

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Plasma Science and Technology
Room: A1 - Session PS1-WeM

Plasma Diagnostics, Sensors, and Control I
Moderator: G. Upadhyaya, Lam Research

8:00am **PS1-WeM1 A New Diagnostic Tool of Electron Energy Distribution Function in Capacitive Mode Plasmas in a Variety of Frequencies**, *H. Shindo, **Y. Nakazaki***, Tokai University, Japan

A new diagnostic tool to measure Electron Energy Distribution Function (EEDF) by an emissive probe has been proposed[1] and applied to radio-frequency (RF) plasmas. In particular, the measurements are made, focused on the condition in which the mode transition from the capacitive to the inductive is occurred at the frequencies of 2 to 60 MHz. It is generally difficult for a conventional probe method to measure EEDF in RF plasmas, because of the plasma potential fluctuation, particularly in the capacitive mode. On the contrary, one of the advantages of the present method is that the measurements are free from the high frequency potential fluctuation.

The method is based on measurement of the functional relationship between the floating potential change ΔV_F and the heating voltage V_H of emissive probe. If the Maxwellian plasma is concerned, a practical and useful equation for ΔV_F can be obtained as in [1]. It is important to know that the value of ΔV_F contains information of electron energy distribution with several electron volt interval along the floating potential V_F, because ΔV_F is determined only by the current of plasma electrons with an energy interval.

In the experiments, the values of ΔV_F were measured in the Ar plasmas which were produced by a single-loop antenna[2] in the frequencies of 2 to 60 MHz and the gas pressures of 5 to 100 mTorr. The values of ΔV_F behave quite differently, depending on the frequency and the gas pressure, hence the plasma mode. It is found that in the inductive mode appeared at the pressures above 20 mTorr at 2 MHz, 30 mTorr at 13 MHz, the value of ΔV_F is consistent with the above-cited equation, enabling to determine the electron temperature, while in the capacitive mode appeared below abovementioned pressures and at 60 MHz, the behavior of floating potential change ΔV_F is fairly complicated, hence non-Maxwellian plasma. In all capacitive modes, from the data set of ΔV_F and V_F, the electron energy probability function (EEPF) is calculated, and the EEPF thus obtained reveals a bi-Maxwellian with the two electron temperatures depending on the frequencies. It should be emphasized that the present diagnostic method becomes powerful in observation of the plasma mode transition in a variety of frequencies.

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8:20am **PS1-WeM2 A Diagnostic Investigation of Pulsed PECVD for Thin Film Deposition**, ***C. Lange***, *C.A. Wolden*, Colorado School of Mines

Low frequency (~1 Hz) pulsed PECVD is an alternative approach for self-limiting growth of high quality thin films at high rate and with good conformality. This technique raises a number of new questions with respect plasma ignition and dynamics. Critical questions include the role of metal precursors in the gas phase as well as those that adsorb to chamber surfaces when the plasma is off. To gain a more fundamental understanding of this process we have built a reactor with a diagnostics suite that includes I-V measurements, Langmuir probe, optical emission spectroscopy (OES), quadrupole mass spectrometry (QMS). In this paper we will present transient measurements from these techniques that are acquired in registry with the plasma pulse waveform. Relevant time scales in this system range from microseconds for application of a stable voltage waveform to seconds for mass transfer and chemical reactions. These critical time scales in the process are experimentally determined. Results will be compared to detail computational models. To decouple the complexities of this process comparisons are made among systems of increasing complexity. These include a baseline O_2/Ar plasma, continuous wave PECVD, plasma-enhanced ALD, and finally pulsed PECVD.

8:40am **PS1-WeM3 Characterization and Active Stabilization of Plasma and Generator Interactions**, *V.L. Brouk*, ***D. Carter***, Advanced Energy Industries, Inc., *J. Roberg*, Advanced Energy Industries, Inc

Plasma instabilities are often seen in low power, low pressure, electronegative discharges. Instabilities affecting particle density, optical emission and coil voltage have been observed with oscillation frequencies ranging from a few hundred hertz to well over one hundred kilohertz [1,2]. While instabilities can be inherent to plasma conditions it is well known that power delivery plays an important role in promoting or propagating the behavior. A study of the mutual interaction between RF amplifier and plasma impedance shows the alignment between impedance trajectory and the power profile contours of the generator is critical in determining a system's sensitivity to instabilities. Reactive elements in the delivery path can be used to rotate impedance trajectories but the recent advent of variable frequency RF supplies has provided a more convenient means for trajectory rotation and active stabilization. In this work we empirically evaluate these behaviors and demonstrate the utility of RF frequency as a controllable parameter for plasma stabilization. In defining an active stability control system, we demonstrate measurements for detecting and quantifying instabilities. Instability oscillation frequency offers insight into the nature of parasitic feedback from mutual generator-plasma interaction and thus we show how discriminating instability frequency is also useful in defining an intelligent stability control system.

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9:00am **PS1-WeM4 Plasma Characterization of a 200-mm Hollow Cathode Magnetron for the Deposition of Metallic and Compound Thin Films**, ***L. Meng***, *R.E. Flauta, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The hollow cathode magnetron (HCM) is a high density plasma tool developed for ionized physical vapor deposition (I-PVD) used for high-aspect ratio thin film interconnects. To better understand the fundamental mechanisms of the HCM device performance and consequently obtain the control to ensure highly conformal and uniform thin film deposition, it is necessary to study the plasma conditions and correlate them to the resultant thin film properties. A commercial high power 200-mm INOVA HCM deposition tool from Novellus was characterized using a 3-D scanning Langmuir probe that was specifically engineered for the intense metal plasma present. This yielded a spatial resolution of both electron density (n_e) and temperature (T_e). In addition, a gridded energy analyzer (GEA) was integrated with quartz crystal microbalance (QCM) to determine the ionization fraction of the metal flux reaching the substrate. With an increasing input power in the range of 0-16 kW, T_e at the substrate decreased from 3 to 1 eV while n_e increased from 6×10^{10} to 2×10^{12} cm^{-3}. A decreasing pressure also increased the electron density. The 3-D spatial distribution of n_e and T_e in the HCM tool revealed a higher n_e and lower T_e at the center of the plasma than at the edge. These results strongly correlated to the resultant film deposition quality and uniformity on the substrate. The deposition rate of metal flux was recorded with QCM, while the GEA was adjusted to repel or admit the metal ions to allow for an ionization fraction of the metal atoms to be calculated. This fraction varied from less than 10% to over 90% depending on the input power and pressure conditions. Lower HCM power increased the ionization fraction due to the corresponding higher T_e and thus higher ionization cross section. At higher pressures, the ionization was enhanced because of the greater residence time of atoms in the plasma. The ion energy distribution was also studied using the GEA/QCM tool. These plasma diagnostics measured the resultant mechanisms of the HCM and provided a matrix of parameters such as T_e, n_e, metal ionization fraction, ion energy and deposition rate to allow for optimization of the deposition process. Ta and TaN thin films were then formed on Si substrates using Ar or Ar/N_2 sputtering plasmas, respectively. These films were characterized through the use of scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to determine the microstructure, crystal quality, and stoichiometry of the deposited film. The film properties were found to be affected by the HCM power, pressure and the sample locations, and correlated with the plasma parameters.

9:20am **PS1-WeM5 Probe Measurements in a Very High Frequency CCP Discharge**, ***L. Dorf***, *S. Rauf, K. Ramaswamy, K. Collins*, Applied Materials **INVITED**

Langmuir probe (LP) measurements in a realistic very high frequency (VHF) capacitively coupled plasma (CCP) discharge are complicated by a number of factors, such as absence of a well-defined DC ground reference and unpredictable behavior of standard electronic components at VHF. The amplitude of RF potential in a VHF CCP discharge can be large (few tens of volts), especially compared to that in an ICP discharge with similar parameters. RF potential distorts both electron and ion parts of the measured probe V-I characteristic, resulting in unrealistic plasma parameters, and therefore needs to be compensated for. Here, we present results of measurements performed in a 300 mm 162 MHz dielectric plasma etcher using a compensated LP (CLP) and a floating double probe (DP). Probe designs employ a number of previously developed techniques. The

probes were used to study the effects of magnetic field, input power, pressure, and chemistry on plasma density radial profiles. The electron part of the CLP V-I characteristic was also used to study the effect of the input power on the electron energy distribution function (EEDF). For all operating conditions – input power of 100 - 1400 W and neutral pressure of 10 - 300 mT – the measured electron temperature was found to lie in the range of 2 - 4 eV, and the plasma density in the range of a few 10^{10} to a few 10^{11} cm^{-3}, increasing with power. In Argon, at 10 – 50 mT, the density was found to increase with pressure (due to higher ionization rate). At higher pressure, 50 – 100 mT, the density profile was found to become more uniform, but no significant change in maximum density was observed; further increase in pressure (100 - 300 mT) leads to a decrease in plasma density. Applying a magnetic field of a few tens of Gauss (generated by solenoidal coils placed above the top electrode) was confirmed to have a significant effect on the radial density distribution. Due to a difference in electron residence time caused by the difference in field lines geometry, edge density increases with magnetic field, whereas center density decreases. In electronegative chemistries, the effects of pressure and magnetic field are different. Namely, in O_2 at 15 – 100 mT: (a) positive molecular ion density decreases with pressure (possibly due to higher attachment), and (b) center density decreases with magnetic field, but edge density remains largely unchanged. In CF_4, the effect of pressure is similar to that in O_2, whereas the effect of magnetic field is like that in Ar at low pressure (15 mT), and like that in O_2 at high pressure (100 mT). Experimental results were found to be in general agreement with results of applicable simulations.

10:40am **PS1-WeM9 Macroscopic Diagnostics for In-Situ Measurement of Sidewall Charging During Plasma Etching**, ***E. Ritz***, *J.A. Hoban, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, the leading type of manufacturing defects that occur are trenching, bowing and twisting. These defects cause failures in semiconductor devices such as processors and DRAM. In order to investigate the role of feature sidewall charging on these defects, a series of macroscopic diagnostics were implemented which are capable of measuring time-resolved charge buildup at several points along a feature profile. This in-situ diagnostic consists of alternating conducting and insulating layers made of copper and teflon, respectively, with an axial hole that acts as the feature via. The insulating layers create discrete measurement layers, provided by the copper electrodes, which can be independently monitored inside of a commercial etching tool in real time to determine how the incident current from the plasma varies along the feature depth. By measuring the current reaching the bottom of the feature, as compared to the mid-plane or the top, one can determine the influence of sidewall charging. To determine the effect of geometry on charging, several aspect ratios were used by maintaining the same device height but varying the diameter of the via. The entire diagnostic is 19.2mm tall with aspect ratios from 5:1 to 10:1. Plasma and charging experiments were conducted in a commercial silicon dioxide etch chamber with three available frequencies (2.0 MHz, 2.2 MHz, and 13.56 MHz) thus allowing study of frequency-dependent charging, as well. Typical powers ranged from 300W to 1000W resulting in sidewall current measurements on the order of milliamps. Typical plasma densities are $2*10^{12} \pm 5*10^{11}$ cm^{-3} and electron temperatures are 3 ± 0.3 eV. Results from the diagnostics are shown for various plasma conditions and compositions.

11:00am **PS1-WeM10 Study on Relation between CFx Radicals and Plasma Parameters in ICP Plasmas with Laser-Induced Fluorescence and Wave Cutoff Probe**, ***J.-H. Kim***, Korea Research Institute of Standards and Science (KRISS), *K. Rho,* KAIST, South Korea, *Y.-S. Yoo, S.-J. You, D.-J. Seong, Y.-H. Shin*, KRISS, South Korea

The behaviors of CF and CF2 radicals were studied in CF4 inductively coupled plasma. CF and CF2 radicals were measured using a laser-induced fluorescence method [1,2]. Absolute electron density was measured using a cutoff probe [3], and the electron temperature was measured using a Langmuir probe to study relation between the electron property and radicals. CF and CF2 densities are drastically changed by variations of operating pressure, ratio of mixed gases and RF source power. To examine the relation between electron density and CF and CF2 radicals, CF, CF2 radical and electron density were measured as varying the RF power which is a major external parameter influencing to the electron density. As the RF power was increased, CF and CF2 radical density increased in the range of low electron density and then decreased over a critical electron density. Dependence of CF and CF2 radical density on the electron density was theoretically analyzed with rate equations. The theoretically analyzed relation between the electron density and the radical density was in good agreement with the experimental result.

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11:20am **PS1-WeM11 Development of High Density Radical Source and the Behaviors of Radicals in N_2-H_2 Mixture Plasma**, ***S. Chen***, Nagoya University, Japan

Dry processes using nitrogen atoms are essential to nitride semiconductor device fabrications such as nitridation, etching damage restoration or nitrogen doping technologies. To reduce the processing time and improve the film quality, the high density radical source with high efficiency and stability is strongly required. So far, some kinds of radical sources have been evaluated and characterized qualitatively using optical emission spectroscopy (OES). However, the absolute density could not be measured by the OES. In this study, we have developed a new high density radical source (HDRS) and measured the absolute density of atomic radicals by using vuacuum ultraviolet absorption spectroscopy (VUVAS).

The HDRS was designed by optimize the number of antenna coil turns in ICP. The ICP with 4 turns coil antenna enabled us to obtain the highest N atomic radical density. It was found that the radical density was significantly dependent on the power density, plasma density and gas temperature. N radical density was increasing from $7.3x10^{11}$ to $3.6x10^{12}cm^{-3}$ with pressure increases from 0.025 to 0.5Pa. These results show the N radical density was one order magnitude higher than traditional source. In the power dependence of radical density, the radical density was increased with increase the powers up to 400W and saturated.

The HDRS was also characterized using N_2-H_2 gas mixture. Relative changes of N, H and NH_3 densities were measured as a function of the N_2 flow rate ratio. NH_3 was measured by Quadrupole Mass Spectroscopy (QMS). In this experiment, the total pressure N_2/H_2 was fixed at 0.5Pa. When N_2/H_2 ratio increased from 10% to 33.3%, the absolute density of H radical was increased from $2.3x10^{12}$ to $4.1x10^{12}cm^{-3}$. Absolute density of N radical increased from $2.3x10^{11}$ to 1.7 $x10^{12}cm^{-3}$. At the N_2/H_2 ratios beyond 33.3%, the N radical density increased to $2.1x10^{12}cm^{-3}$, but H density decreased to $3.2x10^{11}cm^{-3}$. In this experiment, the behaviors of NH_3 relative density agreed with those of H radical. When the N_2 flow rate ratio of 33% was fixed and the pressure was varied from 0.025 to 0.35Pa, it was found that the H radical density was higher than N radical density, but at pressures of above 0.35Pa the N radical density increased rapidly to $5.1x10^{11}cm^{-3}$ and H radical density increased to $3.4x10^{11}cm^{-3}$. As a result, the behaviors of radicals in N_2-H_2 mixture plasma were investigated and the mechanism of radical kinetics in HDRS was discussed.

Plasma Science and Technology
Room: B2 - Session PS2+TF-WeM

Plasma Deposition and Plasma-assisted ALD
Moderator: E.R. Fisher, Colorado State University

8:00am **PS2+TF-WeM1 Plasma Polymerization of bis-1, 2-(triethoxysilyl) Ethane (BTSE): Interfacial Characterization by ToF-SIMS and XPS**, ***A. Batan***, Univ. Libre de Bruxelles, Facultés Univ. Notre-Dame de la Paix, Belgium, *N. Mine, B. Douhard,* Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Brusciotti, I. De Graeve, J. Vereecken,* Vrije Univ. Brussel, Belgium, *M. Wenkin, M. Piens,* Coating Research Inst., Belgium, *H. Terryn,* Vrije Univ. Brussel, Belgium, *J.J. Pireaux,* Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Reniers*, Univ. Libre de Bruxelles, Belgium

Plasma polymerized BTSE films were deposited by vacuum and atmospheric plasma on aluminum (99.99%) substrate. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for probing the metal/film interface. Ion etching by Xe+ 500 eV and 250 eV, depending on the plasma polymer BTSE film thickness, exposed the interfacial region, while Ga+ (15 keV) ions analysed the material composition.

An AlOSi+fragment was identified at nominal mass m/z = 70.9539 amu in high mass resolution spectra. The presence of this aluminium-oxygen-silicon ion fragment is a strong indication of an existing chemical interaction between the plasma polymer BTSE film and the aluminum substrate: the nature of this interaction implies the formation of a covalent bond between the silane and the aluminum substrate. Until now, this strong interaction silane-aluminum has never been observed in plasma polymer BTSE films.

Ageing tests combined with X-ray photoelectron spectroscopy measurements allowed the evaluation of the adhesion performance of plasma polymerized BTSE films on aluminum. The Si2p signal intensity was measured before and after dipping the coated sample in an ultrasonic water bath for 30 min, at room temperature. The Si2p peak intensity remained constant after the sonication test, showing a strong adhesion between the deposited layer and the aluminum substrate.

Acknowledgements

The project partners VUB, ULB, FUNDP and CoRI gratefully acknowledge the Belgian Science Policy for funding the FOMOS project (P2/00/04) in the "Programme to stimulate knowledge transfer in areas of strategic importance". www.belspo.be

8:20am **PS2+TF-WeM2 Self-limiting Deposition of Nanolaminates by Pulsed PECVD**, *P.C. Rowlette*, ***C.A. Wolden***, Colorado School of Mines

Self-limiting synthesis of alumina-titania nanolaminates (ATO, Al_2O_3/TiO_2) was accomplished via pulsed plasma-enhanced chemical vapor deposition. At the synthesis temperature of 150 °C the alumina layers were amorphous, while TiO_2 layers displayed a polycrystalline anatase structure. Digital control over nanolaminate structure was demonstrated through elemental analysis and TEM imaging. The optoelectronic properties of the ATO structures were examined as a function of composition and bilayer thickness. C-V measurements showed that the effective dielectric constant (κ) of the nanolaminates was consistent with treating the structure as individual capacitors in series. I-V measurements showed that leakage current deteriorated with TiO_2 content, though low leakage was restored through interfacial engineering. With respect to dielectrics these results suggest that the best nanolaminate would employ Al_2O_3 interface layers deposited by PE-ALD to minimize leakage current, and that these two layers would sandwich a single TiO_2 layers whose thickness would set the effective dielectric constant. We will also present work in SiO_2 –TiO_2 nanolaminates formed by the same technique at room temperature with applications as optical components. Finally, we will present recent findings in the area of inorganic/organic hybrid nanolaminates formed by alternating oxide and polymer layers.

8:40am **PS2+TF-WeM3 Tailoring PECVD Ultra-Low-k Films for Nanoscale Interconnects**, ***E.T. Ryan***, GLOBALFOUNDRIES, *S.M. Gates, S. Cohen, Y. Ostrovski, V. Patel, E. Simonyi, C. Dimitrakopoulos,* IBM T.J. Watson Research Center, *A. Madan,* IBM Microelectronics, *G. Dubois,* IBM Almaden Research Center, *A. Grill*, IBM T.J. Watson Research Center **INVITED**

Ultra-low-k (ULK) insulating films are critical to reduce the resistance-capacitance (RC) delay in interconnect wires. This talk will briefly review the history of low-k materials that culminated with ULK nanoporous organosilicate glass (also called pSiCOH) films deposited by plasma-enhanced chemical vapor deposition (PECVD).

Nanoporous ULK pSiCOH films pose many interconnect fabrication challenges, and the needs of integration impose limits on the material properties of the films. For example, the pSiCOH film can be damaged by exposure to other plasma processes, and the degree of damage is related to material properties such as porosity, pore size, pore interconnection, carbon content, and bonding arrangement.

The stress and mechanical strength (modulus) of the pSiCOH film is critical for the structural stability of the interconnect wires. Spontaneous cracking is directly related to both modulus and stress. Packaging imposes additional stresses on the interconnect lines. Furthermore, if the modulus of the ULK film becomes too low, capillary forces during post-etch wet cleaning can cause the patterns in the pSiCOH film to collapse.

These integration needs require balancing various trade offs in material properties, and this constrains the process space for pSiCOH film deposition. The talk will review our work to design pSiCOH films with different properties to meet different integration needs. Examples of PECVD films with properties tailored to meet these interconnect needs illustrate the trade offs we face.

First we review our efforts to design films that are resistant to damage by the plasmas used for etch and ash and cap deposition. Mechanical properties were also maintained at favorable values. We modified a conventional pSiCOH film (V1) prepared from DEMS and BCHD porogen by adding a carbosilane skeleton precursor to incorporate new carbon structures. The modified films (V2, V3) can be adjusted by the choice of the carbosilane precursor. The films were characterized for electrical and mechanical properties, pore characteristics, and FTIR. The plasma damage of the films was characterized by thickness loss after HF etch of the damaged layer and depth profiling by ToF-SIMS. The new pSiCOH V2 and V3 films show reduced plasma damage. Our effort to optimize the pSiCOH modulus will be discussed, with the overall goals of reducing plasma induced damage and maintaining favorable stress and modulus.

9:20am **PS2+TF-WeM5 Amplitude Modulated Pulse RF Discharges for Producing and Driving Nano-Blocks**, ***S. Iwashita****, *H. Miyata, H. Matsuzaki, K. Koga, M. Shiratani*, Kyushu University, Japan

We have proposed a bottom-up nanosystem-fabrication method, which consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, transport of nano-blocks towards a substrate, their arrangement on the substrate using pulse RF discharges with the amplitude modulation (AM) of the discharge voltage. For the method, control of the size of nano-blocks and their manipulation without their agglomeration are important. Up to now, we have succeeded in controlling the size of nano-blocks by pulse RF discharges,[1] and have realized their rapid transport from their generation region towards a substrate with suppressing agglomeration by pulse RF discharges combined with AM.[2,3] Here we report a criterion for driving nano-blocks rapidly and discuss their transport mechanisms.

Experiments were carried out using a capacitively coupled RF discharge reactor described elsewhere.[1-3] Nano-blocks were formed in 13.56 MHz RF discharges of $Si(CH_3)_2(OCH_3)_2$ diluted with Ar. Nano-block transport in AM discharges is classified into two kinds: one is the rapid transport at a velocity more than 60 cm/s during the modulation period and the other is the slow transport at a velocity of 3-5 cm/s after turning off discharges due to temperature gradient. The key parameters to the rapid transport are the period Δt and voltage V_{AM} of the modulation and asymmetry of the discharges, which is characterized by the dc self-bias voltage V_{dc}. The larger nano-blocks need longer Δt, higher V_{AM}, and higher V_{dc}, for their rapid transport because of their large inertia. All nano-blocks of 26 nm in size, for instance, are transported rapidly during the modulation period for V_{dc} = -412 V, Δt = 100 ms and V_{AM} = 1076 V, while 54 % of them transported rapidly during the modulation period and 46 % of them are transported after turning off discharges for V_{dc} = -350 V, Δt = 100 ms and V_{AM} = 883 V. Just after the initiation of the modulation, electrostatic force drives nano-blocks, and then ion drag force drives them towards a substrate. It should be noted that although most nano-blocks are neutral, some of them turn into ones charged negatively due to charge fluctuation and such nano-blocks charged negatively are driven by electrostatic and ion drag forces. The method was applied to deposition of nano-block composite porous low-k films and dielectric films of k = 1.4 and Young's modulus above 10 GPa were realized.

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9:40am **PS2+TF-WeM6 Plasma Deposition of Platinum-Based Nanocomposite Films as Fuel Cell Electrocatalysts**, ***A. Milella***, *E. Dilonardo,* University of Bari, Italy, *F. Palumbo,* Institute for Inorganic Methodologies and Plasmas (IMIP)- CNR, Italy, *S. Martin,* CEA-G/ Leti, France, *R. d'Agostino, F. Fracassi*, University of Bari, Italy

In Proton Exchange Membrane Fuel Cells (PEMFC) the electrode reactions rely heavily on the use of platinum catalysts. Since cost of this precious metal is one of the main barriers for commercialization of fuel cells, many research efforts are addressed to obtaining higher catalytic activity than the standard carbon-supported platinum particle catalysts used in current PEM fuel cells, with a reduced amount of metal. In this framework, plasma processes are particularly appealing since they allow the dispersion of catalyst in form of nanoparticles and the control of the film thickness to the nanometer scale. Few examples are present in literature concerning the use of low pressure plasma for platinum-containing films as catalytic electrodes.

In this contribution we report our latest results on the one-step deposition of nanocomposite thin films containing platinum nanoclusters (high specific area), with definite concentration and uniform in size. Thin films are obtained from a simultaneous plasma-enhanced chemical vapour deposition of ethylene (C_2H_4) / argon gas mixtures and RF sputtering of a platinum target. The main advantages of this approach consist in the reduced thickness (less then 1 micron), the possibility to coat complex shapes, and the easy scale up in a continuous process. A comprehensive study on the effect of different parameters (RF power, deposition time, gas flow rates) on the film chemical composition and structure will be presented. In particular, it will be shown that the platinum content in the film, determined by X-ray Photoelectron Spectroscopy (XPS), can be continuously varied by properly controlling the RF power and the monomer flow rate. Field Emission Gun-

* PSTD Coburn-Winters Student Award Finalist

Scanning Electron Microscopy (FEG-SEM) shows that films are porous with a cross-section characterized by columnar structures of different size and orientation, depending on the deposition parameters. Transmission Electron Microscopy (TEM) confirms that platinum aggregates in crystalline nanoclusters of diameters in the range 3-7 nm, uniformly distributed in the film. The electrochemical active area of the films, as determined from *ex-situ* Cyclic Voltammetry (CV) analyses, reaches a maximum correspondingly to a platinum load of about 60%. Preliminary results on device testing will be also presented.

Acknowledgments

This work was founded by the European Project *NAPOLYDE* (NMP2-CT-2005-515846).

10:40am **PS2+TF-WeM9 Contribution of CN Radicals to the Nitrogen Content of Plasma-Deposited a-CN$_x$ Materials**, ***J.M. Stillahn****, *E.R. Fisher*, Colorado State University

This work details our efforts to explore the plasma-enhanced chemical vapor deposition of amorphous carbon nitride (a-CN$_x$) materials, which exhibit a variety of interesting physical and chemical properties. These properties depend critically on the manner and extent to which nitrogen is substituted into the amorphous film network, but the mechanisms responsible for nitrogen incorporation are often obscured by the complexities of mixed-precursor systems (e.g., CH_4/NH_3) that are frequently used to study a-CN$_x$ deposition. Single-source precursors (e.g., CH_3CN, BrCN) help to simplify the gas phase chemistry, and in this work we have employed such precursors to learn about nitrogen incorporation mechanisms in more complex systems. The CN radical is examined with particular interest as it exhibits near-unity surface reaction probabilities under all conditions, providing a stark contrast with other N-containing plasma species such as the less-reactive NH radical. Interestingly, this difference in surface reactivity is echoed by disparities in the molecules' internal energies, which are characterized in this work by the rotational temperature. The contributions of the CN radical become especially evident with the use of BrCN plasmas, yielding films that delaminate and buckle upon exposure to atmosphere. This behavior may reflect a high concentration of terminating groups in the film, leading to a porous material that is compressively stressed as it absorbs water. Data such as these can be used to form a more complete understanding of the chemical mechanisms that lead to a-CN$_x$ deposition.

11:00am **PS2+TF-WeM10 Comparison between a DC Reactive Magnetron Sputtering Discharge in an Ar/NH$_3$ and Ar/H$_2$/N$_2$ Gas Mixture**, ***F. Henry***, *A. Batan, F. Reniers*, Université Libre de Bruxelles, Belgium

The reactive magnetron sputtering technique is widely used for thin films deposition. This one offers many advantages like: a large choice of composition of the deposited films, a low temperature of deposition that allows to use a large scale of substrates and a high speed of deposition. Other techniques used for thin films deposition like CVD often required the use of hazardous gases and required a high temperature of deposition.

In this study, two different gas mixtures (Ar/NH_3 and $Ar/H_2/N_2$) used for the deposition of silicon nitride thin films were compared. Optical Emission spectroscopy spectrum (OES) were recorded to characterize the plasma gas phase. X-ray Photon-electron Spectroscopy (XPS) was used to determine the stoichiometry of the deposited thin films and used to perform a depth profiling of the silicon target after exposure to the reactive magnetron sputtering discharge. Optical interferometry was used to measure the film thickness and current-voltage curves were plotted to determine the electric characteristics of the discharge.

The influence of the plasma parameters such as the molar fraction of reactive gas and the total pressure was studied. The same parameters were investigated for both kind of gas mixture and a detailed comparison was performed.

The experiments were performed in a stainless steel chamber equipped with a home-made magnetron cathode. The total pressure was set between 5 x 10^{-3} Torr and 2 x 10^{-2} Torr and the molar fraction varied between 0 and 0.6 in reactive gas. During all experiments the discharge current was set to 300 mA.

The excited species detected into the Ar/NH_3 and $Ar/H_2/N_2$ plasma were the same, except for the NH radical that was not detected in the $Ar/H_2/N_2$ plasma.

The stoichiometry of the thin films deposited with the two kind of gas mixtures was investigated by XPS, a N/Si ratio of 1.33 was determined for the $Ar/H_2/N_2$ plasma and 1.22 for the Ar/NH_3 plasma.

The current voltage curves were plotted at different molar fractions of reactive gas and at different total pressures. A typical drop of the tension due to a poisoning of the target was observed for the Ar/NH_3 plasma and for the $Ar/H_2/N_2$.

11:20am **PS2+TF-WeM11 The Application of AC Diode Sputtering for Aluminum Thin Films in Small Apertures**, ***D.R. Walters***, Argonne National Laboratory

A thin conductive film was applied on the inner surface of a small-aperture vessel using the AC Diode Sputtering process. This paper describes the process and the technical equipment used in this thin-film method. The process configuration presented here employs a dual-electrode arrangement, which creates a glow discharge field around both electrodes, thereby spreading out the affected area. An example of coating performed in a 5 mm by 12.5 mm rectangular channel by 3.4 m in length is present along with examples of circular cross-sectional channels. A significant challenge of this configuration is how to get a homogeneous pressure throughout a long constricted channel; results show that the dual inlet-output gas flow circuit was able to achieve the constancy needed for a satisfactory film. Analyses of the sample films confirm acceptable uniformity even in the pressure region of 600 mTorr. Further work has shown that the glow discharge can be maintained into a pressure regime of greater than 10 Torr.

11:40am **PS2+TF-WeM12 3D Plasma Simulations of a High Density Plasma CVD Reactor using VIZGLOW**, ***P. Kothnur***, *R. Kinder*, Novellus Systems, Inc., *X. Yuan*, Esgee Technologies, Inc., *L. Raja*, The University of Texas at Austin

High-density plasma CVD (HDP-CVD) reactors are used to provide void-free gap fill of high-quality dielectric films in high aspect ratio device structures. The ability to accurately model a prototype or development design is a necessary capability of any equipment manufacturer in order to lower cost and shorten design cycle times. However, the ability to model an HDP-CVD tool accurately remains a difficult challenge due to the complex coupling of power deposition and plasma transport in a CVD chamber. To investigate issues related to power deposition and electron transport, we have used the VIZGLOW simulation software developed at Esgee Technologies to simulate 3D geometries. The simulation software enables the solution of the energy equation for electron temperature, while solving for the electron density and electrostatic fields through a quasi-neutrality condition. Electron heating is produced by electromagnetic fields, while the energy equation is solved for all heavy species. The HDP-CVD tool considered is a hemispherical inductively coupled plasma (ICP) source. The simulation results are compared to previously published experimental measurements with Langmuir probes, voltage and current monitors, optical emission spectroscopy, ion mass spectrometry, and gas quadrapole mass spectrometry. Furthermore, results from VIZGLOW are benchmarked against simulation results obtained from the Hybrid Plasma Equipment Model (HPEM). Results for experimentally measured process gases (Ar, Ar/O_2, $Ar/O_2/H_2$) at low pressures (< 15 mTorr), operating at 3-6 kW's of input power, and varying rf frequency (400 kHz –13 MHz) are discussed.

* PSTD Coburn-Winters Student Award Finalist

Plasma Science and Technology
Room: A1 - Session PS1-WeA

Plasma Modeling
Moderator: M. Shen, AMAT

2:00pm **PS1-WeA1 Plasma Prize Lecture - Modeling and Simulation of Microplasma Discharges**, ***D.J. Economou****, University of Houston **INVITED**

High pressure (100s of torr) microplasma (length scale 100s of microns) discharges have potential applications as chemical microreactors, sensors, microelectromechanical systems (MEMS), and excimer radiation sources. Modeling and simulation of these systems, combined with plasma diagnostics, can provide critical information on fundamental discharge characteristics, and help extend the window of stable microdischarge operation. This talk will review the modeling and simulation methodologies used for microplasmas, with special emphasis on the coupling between plasma and neutral gas flows. The effect of operating conditions on gas temperature and in turn on discharge characteristics will be discussed in detail. Similarities and differences in modeling and operating characteristics between microdischarges and macroscopic discharges will be detailed. Simulation predictions will be discussed in light of spatially resolved plasma diagnostics used to measure important microdischarge properties (electron density and temperature, gas temperature, excited state densities, electric fields, etc.).

Work supported by the Department of Energy and the National Science Foundation

2:40pm **PS1-WeA3 Feature Scale Modeling of High Aspect Ratio Dielectric Etch**, ***P.J. Stout***, *J.A. Kenney, S. Rauf*, Applied Materials

Discussed will be results of three dimensional feature scale modeling of high aspect ratio (HAR) dielectric etching. The feature model is coupled to a reactor model which supplies specie flux values and angle and energy distribution functions to the feature model. The feature model has been used to study the mechanisms which contribute to the HAR etched profile. The mechanisms in the model include etchant transport to the surface, specular and diffusive reflection within the feature, adsorption, surface diffusion, energy loss, deposition, and etching. Typical requirements for HAR dielectric etch include reduction of profile bow, no off-axis profiles (i.e twisting, tilting), large bottom cd's, and no bottom profile distortion or rotation. Mechanisms contributing to off-axis etch profiles and bottom distortion will be discussed including mask shape, polymer deposition, etch by products, off-axis ion incidence, and yield curves. The effect of source power, bias power, and frequency mixing on the etched profile will also be explored. The shape of the mask at the opening controls the amount and direction of etchants entering the feature. Thus, the shape and evolution of the feature mask opening plays a large role in the evolution of the etched profile. For instance, a more angled mask increases the bow of the etched profile for a fixed process. Mask shape influences how polymer builds up at the opening and how the hard mask facets at the opening. Polymer buildup at the feature lip alters the path of striking ion incident near the feature opening. Facets forming at the feature opening also steer a portion of incoming ion flux from their largely wafer normal trajectory inside the feature. So the evolution of the mask shape over the course of the etch influences the ion trajectories and neutral shadowing to the etch front changing the character of the etched dielectric profile as the etch process proceeds.

3:00pm **PS1-WeA4 Feature Profile Evolution: From Plasma Etching and Deposition to Surface Roughness Formation and its Propagation**, *J. Hoang*, ***J. Chang***, University of California, Los Angeles

The limit of current integrated circuit device sizes is defined by state of the art processing technology, including the interplay between photolithography and pattern transfer by plasma etching. These two processes have a convoluted relation among complex surface kinetics, physical dependencies, and gas phase flux distributions that define the evolution of surface features. In this work, a model is developed to investigate the feature profile evolution during deposition and etching with a focus on roughness formation and its propagation. Surface kinetics is based on a translated mixed layer model (TMLM) develop by Kwon et. al.[1] and is implemented in a 3D Monte Carlo simulation domain. Ion incident angle dependence and an elliptical energy deposition model were used to capture the effects of surface morphology on the profile evolution under the bombardment of energetic and directional ions. Species fluxes are determined from experiments or through a reactor scale model.[2] Specifically, we examine chlorine-based plasma etching and how passivating species affect roughness formation through modification of the local surface composition. A translated mixed layer kinetics model is fitted to chlorine plasma beam etching experiments on silicon dioxide, and the reaction parameters are extracted to determine the relative etch yield on partially oxidized surfaces. Atomic force microscopy measurements of chlorine plasma etched Si with varying amounts of O_2 addition in the feed gas are compared to the simulated roughness and show qualitatively good agreement. For ionized deposition, we investigate the effects of roughness and geometry on the deposition conformality. The directionality of the ions along with the extent of physical sputtering is investigated and extracted from experimental SEM images. These parameters are then incorporated into the feature scale model, where the effects of propagation and geometry are investigated and show reasonable agreement with the observed SEM images.

[1] Kwon et al. Journal of Vacuum Science and Technology A. 24(5) 2006

[2] Hsu et al. Journal of Vacuum Science and Technology B. 26 (6) 2008

4:00pm **PS1-WeA7 Three-Dimensional Modeling of Ion Angular and Energy Distributions in Capacitively Coupled Plasmas**, ***J.A. Kenney***, *P.J. Stout, S. Rauf, K. Collins*, Applied Materials

As high aspect ratio (HAR) etch requirements continue to grow more stringent, it has become increasingly important to understand the influence of reactor design and process conditions on three closely intertwined areas: plasma uniformity; fluxes, energies, and angular distributions of species exiting the plasma and impinging on the wafer; and profile evolution of the HAR features. Due to the complexities and uncertainties involved in experimental analysis of these topics, many modeling efforts have been directed at each. Here, we investigate the unique aspects arising when each realm is considered fully in three dimensions in the context of a capacitively coupled plasma (CCP) reactor, with an emphasis on ion angular and energy distribution functions (IAEDFs).

Our efforts include a three-dimensional fluid plasma model, a Monte Carlo-based particle simulation for charged species, and a three-dimensional Monte Carlo-based feature profile evolution tool. The plasma model provides spatially and temporally-resolved species densities, species fluxes, and electric fields. The particle simulation uses that information in turn to generate ions in the bulk plasma and track them as they are influenced by the time-varying electric fields as well as collisions with other species. The energy and three-dimensional angle for ions striking the wafer are recorded and binned as appropriate. The feature profile evolution tool uses this data along with the species fluxes from the plasma model as inputs and includes a variety of physics and chemistry, including ion-enhanced etching, ion sputtering, ion scattering, etch product desorption, and the formation of surface layers.

In this work, we demonstrate the influences of externally applied magnetic fields and azimuthally asymmetric reactor components in CCP systems on the resulting IAEDFs. To isolate the impact of these features, we consider simple etch-relevant feed gas mixtures (Ar, Ar/CF_4, Ar/O_2) and single (162 MHz) and dual frequency (2/60 MHz) configurations. We analyze both the differences between the IAEDFs generated with and without these features as well as differences found between locations within a single wafer. We then examine the linkage between these differences and the results from the feature profile evolution tool.

4:20pm **PS1-WeA8 A Global (Volume Averaged) Model of the Chlorine Discharge**, *E.G. Thorsteinsson*, ***J.T. Gudmundsson***, University of Iceland

A steady state global (volume averaged) model is developed for the chlorine discharge using a revised reaction set [1]. Various calculated plasma parameters are compared to measurements found in the literature, showing a good overall agreement. The reaction rates for the various reactions are evaluated in the pressure range 1 - 100 mTorr. In particular we explore the dissociation process as well as the creation and destruction of the negative ions Cl^-. The discharge is highly dissociated throughout the pressure range explored, 1 - 100 mTorr, even when the absorbed power is low. The mechanism for Cl creation is complex, although electron impact dissociation dominates with roughly 50 - 60 % contribution. Dissociative electron attachment is also of importance and mutual neutralization is an important contributor to the production of Cl atoms at higher pressure. The electronegativity increases rapidly with decreasing dissociation fraction since the Cl- ions are created entirely by dissociative electron attachment, predominantly from $Cl_2(v=0)$, but also up to 14 % from $Cl_2(v>0)$ at 100

* 2008 Plasma Prize Winner

mTorr. The negative ion Cl^- is lost almost entirely through mutual neutralization with Cl_2^+ at high pressure while Cl^+ has a significant contribution at low pressure. Furthermore, the dilution by argon was explored. Dilution by argon decreases the electronegativity but increases the electron temperature, dissociation fraction and the fractional density of Cl^+ ions significantly.

[1] E. G. Thorsteinsson and J. T. Gudmundsson, A global (volume averaged) model of the chlorine discharge, Plasma Sources Sci. Technol., submitted 2009

4:40pm **PS1-WeA9 Characterization of Very High Frequency Capacitively Coupled Plasmas**, ***K. Bera****, L. Dorf, S. Rauf, K. Collins*, Applied Materials, Inc.

As semiconductor technology progresses to the 22 nm node, it is becoming increasingly important to fundamentally understand plasma etching processes and apply this understanding to development and improvement of plasma etch equipment. Capacitively coupled plasmas (CCP) have been widely used for dielectric plasma etching. The general trend in recent years has been towards the use of multi-frequency CCPs which include rf sources in the very high frequency (VHF) regime. We characterize one such system in this paper using two/three-dimensional (2/3D) plasma modeling. Modeling results are validated using experimental data for different operating conditions. Plasma simulations have been performed using our in-house 2/3D fluid plasma model. To account for electromagnetic effects at VHF, this 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. Model validation is performed using radially-resolved electron and ion densities and electron temperature measured with single and double Langmuir probes [1]. Ion density profiles obtained with both probes are generally similar over the range of conditions investigated. Plasma simulations were performed for a wide range of operating conditions [gas pressure (50 – 150 mT), rf power (100 – 1000 W), gases (Ar, O_2, CF_4)] at 60 and 162 MHz with and without a spatially inhomogeneous magnetic field. In agreement with experimental data, we observe that plasma density increases with pressure in Ar while the bulk plasma electron temperature is almost invariant. Plasma density is substantially higher at the higher frequency of 162 MHz. Plasma density is lower in electronegative gases than Ar under identical conditions. Plasma profile changes substantially with application of magnetic field, and the effect of magnetic field is weaker at higher pressures. While electromagnetic effects are strong at 162 MHz, reactor design determines the relative importance of electromagnetic vs. electrostatic effects at 60 MHz.

[1] L. Dorf et al., 2009 AVS Symposium.

5:20pm **PS1-WeA11 Investigation of Standing Wave Formation in the Large Area Capacitively Coupled RF Driven Processing Plasma Source**, ***S.H. Lee****, M.S. Choi, G.H. Kim*, Seoul National University, Republic of Korea

Large area capacitively coupled plasma (CCP) sources are widely used in etch and deposition processes for the fabrication of flat panel display and solar cells. In general, the plasma density may increase with increasing frequency and it may improve the process rate. However the wavelength reduces with increasing frequency and the field variation on the substrate becomes serious due to the formation of standing wave pattern on the electrode. It causes the difficulty to control the process uniformity for the large process area. Many experimental investigations have been carried out for intermediate size plasma source as 1m x 1m and the wave patterns are observed. However, in practice, the reactor size becomes more than 2m x 2m with 13.56 MHz or higher RF frequency. Thus the standing wave effects are issued on the development of large area plasma process. The mechanism of standing wave formation and measurement are the theme of this study. Transmission line and wave models were developed to investigate the standing wave effect, skin effect, and telegraph effect, which have been reported separately. Here the new 1 D analytic model is introduced to describe the formation of standing wave on the reactor of 1.4m x 1.6m with applying 60 MHz, which consists of the transmission line model adapted to analysis of wave pattern from the matcher to the electrode and the wave propagation model for the formation of standing wave between sheath boundary and conducting electrode. Strategically, the wave conditions obtained from the transmission line model are adapted to the boundary values for the wave model. From this model, it reveals that the standing wave formation is related to the structure between the electrode and matching units as well as plasma property. Experimentally, the amplitude of plasma potential fluctuation was monitored from Langmuir probe measurement, being compared to the prediction of wave pattern from the model. It shows fairly good agreement between the model and the measurement. As expected, with increasing the plasma density, the wavelength becomes decreased due to shortening of the sheath thickness. Further results will be presented.

Plasma Science and Technology
Room: B2 - Session PS2+MN-WeA

High Aspect Ratio and Deep Etching for 3D Integration and Memory
Moderator: S. Hamaguchi, Osaka University, Japan

2:00pm **PS2+MN-WeA1 Advanced DRIE Via Etching**, ***F. Gao****, D. James, K. Kolari, J. Kiihamäki,* VTT Technical Research Centre of Finland*, M. Muggeridge*, Aviza Technology, Inc.

We present 3 different types of interconnection vias fabricated by deep reactive ion etching (DRIE) on silicon substrates. One type of vertical vias with 30µm diameter mask opening are etched through 400µm thick wafer by switched Bosch process, featured by very fast etch rate at about 6µm/min and over 12:1 aspect ratio. The other type of vertical vias are tested on smaller diameters ranging from 1-9µm and etched to 20-50µm deep. Those vias have the minimum undercut and smooth sidewalls achieved by non-switched etching. Another type of tapered vias with 75µm mask opening are etched isotropically in DRIE resulting in over 150µm deep vias with 70-80 degree tapering. Silicon etch selectivity against different mask materials are studied and compared for the vertical vias. Thick resist is thought to be better mask to minimize undercut and via top erosion by reflected ions. Tapered vias have the problem of sidewall roughness from the isotropic etch. Both plasma cleaning and argon annealing methods are tested to smooth the silicon sidewalls in the tapered vias.

2:20pm **PS2+MN-WeA2 The Generation and Removal of Heat during DRIE of High Aspect Ratio Structures in SOI with Buried Cavities**, ***J. Dekker****, F. Gao, J. Kyynäräinen, J. Kiihamäki*, VTT Microelectronics Research Center of Finland

This work examines the accumulation of heat and resulting increase in local temperature and loss of selectivity which may occur when etching high aspect ratio structures in SOI wafers with buried cavities. It is shown that unlike high-load, high-rate etches treated elsewhere, in the case of HAR etches the heat is generated mainly by ion-bombardment. Due to the presence of a cavity beneath the structures being released, which typically include a mass suspended by springs, the heat may only be conducted laterally away from the released structures to the surrounding device layer. During the final stages of DRIE etch and overetch, the heat flow from suspended masses is therefore restricted to occur along the springs which attach the mass to the surrounding device layer. The limited heat conductance of long meander springs in particular is unable to remove the heat generated in suspended structures. As a result, the temperature of the suspended structures increases resulting in reduced fluorocarbon depositon upon them. That, in turn, results in a locally increased etch rate of the oxide mask on the suspended structures. The effects of releasable thermal anchors, which provide additional paths for heat conduction away from the suspended mass and therefore aid in the removal of heat, is also discussed.

2:40pm **PS2+MN-WeA3 Ion Trajectory Prediction at High-Aspect-Ratio Hole Etching by the Combination of On-Wafer Monitoring and Sheath Modeling**, ***H. Ohtake****, S. Fukuda, B. Jinnai,* Tohoku University, Japan*, T. Tatsumi,* OKI Semiconductor Miyagi Co., Ltd., Japan*, S. Samukawa*, Tohoku University, Japan

The abnormal etching profiles, such as bowing, etch stop and twisting, have been reported at high-aspect-ratio hole etching. To avoid the failures, we have to predict the ion trajectory and etching profile precisely by analyzing the sheath area around the hole. In this presentation, we developed the ion-trajectory prediction system at high-aspect-ratio hole by combining the on-wafer monitoring technique and sheath modeling for explaining and predicting the etch stop and twisting. Since our developed on-wafer sensors provide the surface potential, the electron density/ temperature and side-wall resistance of the hole, we can simulate the distribution of electric field in the hole. This system revealed that the sidewall conductivity strongly affects the charge-up and ion trajectory in the high-aspect-ratio hole. It also predict the etch stop and twisting phenomena. Consequently, we believe this prediction system is an effective tool for developing the nano-scaled fabrication.

3:00pm **PS2+MN-WeA4 Enhancement Mechanism of Distortion and Twisting in Ultra High Aspect Ratio Dielectric Etching**, ***H. Mochiki,*** Tokyo Electron AT Ltd., Japan*, K. Yatsuda,* Tokyo Electron Ltd., Japan*, S. Okamoto, F. Inoue*, Tokyo Electron AT Ltd., Japan

It is required to fabricate capacitors with aspect ratio of from 40:1 to 60:1 for DRAM at hp 3x nm and beyond generation, and etching such ultra high aspect cylindrical shapes without distortion and/or twisting is the most difficult challenge. Recently, it has been reported that distortion and twisting were caused by electron shading effects, electrical potential difference between the top and bottom of dielectric during plasma etching. In this paper, we report how distortion and twisting are enhanced, and how they can be minimized.

First of all, electron shading effects are results of electrostatic charge on the surface of etched dielectric material – silicon dioxide, and organic capacitor mask is negatively charged where silicon dioxide surface is positively charged. At these generations, DRAM devices are so largely scaled that their capacitors need to be fabricated very close to each other. Consequently, incident positively charged ions in a cylinder, accelerated by plasma sheath, receive repulsive force from not only the cylinder surface itself but also neighboring cylinder surfaces. We confirmed that grad of distortion and twisting changed by altering the layout of capacitors.

On the other hand, we found that distortion and twisting could also be generated from the very beginning of etching at the low aspect ratio portion by observing the top view of a cylinder every 100 nm-deep from the wafer surface. Moreover, we affirmed that distortion strongly correlated with capacitor etch mask profile when varying it on purpose by changing mask etch conditions. Thus, we clarified that another enhancement mechanism of distortion existed apart from electron shading effects.

Therefore, there are several enhancement mechanisms of distortion and twisting, and it is necessary to address each solution. We divided the enhancement mechanisms of distortion and twisting into two modes, which are generated at low and high aspect ratio, and examined their solutions from the etching point of view, respectively. We conclude that the optimization of capacitor etch mask profile was the most effective solution at the low aspect ratio mode, and higher dissociation plasma with relatively higher plasma density and superimposed DC on CCP (capacitively coupled plasma) improved distortion and twisting at the high aspect ratio mode.

4:00pm **PS2+MN-WeA7 High Rate Deep Si Etching for TSV Applications**, ***I. Sakai,*** *N. Sakurai, T. Ohiwa*, Toshiba Corporation, Japan **INVITED**

Si etch process for etching deep and high-aspect ratio structures has been studied intensely for applications such as DRAM trench capacitors and MEMS devices. Recently, there is focus on Si etching for TSV (through Si via) applications for 3-D (three-dimensional) LSIs. Dimensions of the TSVs which are being investigated today vary widely, depending on its application and integration scheme. For example, TSV for 3-D packaging of logic devices may be sub-micron to a few microns in diameter and about 10 microns deep. On the other hand, TSVs used in stacking memory devices, the via diameter and depth would be several tens of microns, and, package for CMOS image sensors using TSVs may have via diameters and depths up to 100 microns.

For TSVs up to 10 microns in depth, the conventional Si deep trench etch process for DRAMs can be easily adapted to etching TSVs because of its similar dimensions. The typical etch rate is several microns per minute. On the contrary, etching of very deep holes of depths on the order of tens of microns and up to 100 microns is not within the experience of conventional front-end LSI fabrication processes. In this case, consequently, an extremely high Si etch rate becomes mandatory because of cost issues, especially for TSV applications which require via holes more than 20 microns deep.

To fulfill this requirement for TSV applications, the Si etch process was investigated focusing on the Si etch rate. First, a large via size of 40 microns was studied, and an etch rate of more than 50 µm/min was realized. It was found that the Si etch rate depended on fluorine radical density, so, high rate was obtained by creating a high fluorine radical density condition by using a high pressure condition of 350 mTorr, with a capacitively-coupled plasma (CCP) reactor with a Dipole-Ring Magnet (DRM) and SF_6 gas chemistry. Furthermore, the etch process for smaller holes of 8 microns was studied to realize high etch rates also. The etch process was modified to obtain a straight etch profile, then, via holes were etched to a depth of 60 microns at an etch rate of 24 µm/min.

High rate deep Si etching is realized for TSV application for holes more than 20 microns deep, using CCP RIE with SF_6–based gas chemistry.

4:40pm **PS2+MN-WeA9 Infinitely High Etch Selectivity and Variation of Line Edge Roughness during Etching of Hard-Mask Layer with Patterned Extreme Ultra-Violet**, ***B.S. Kwon,*** *J.S. Kim, C.R. Jung, J.S. Park, W. Heo, N.-E. Lee,* Sungkyunkwan University, Korea*, S.K. Lee*, Hynix Semiconductor, Republic of Korea

In the nano-scale Si processing, patterning processes based on multilevel resist structures becoming more critical due to continuously decreasing resist thickness and feature size. In particular, highly selective etching of the first dielectric layer with resist patterns and control of critical dimension (CD) and ling edge roughness (LER) are of great importance. In this work, process window for the infinitely high etch selectivity of silicon oxynitride (SiON) layers to EUV resist and variation of LER of extreme ultra-violet (EUV) resist was investigated during etching of SiON/EUV resist in a $CH_2F_2/N_2/Ar$ and $CH_2F_2/N_2/O_2/Ar$ dual-frequency superimposed capacitive coupled plasma (DFS-CCP) by varying the process parameters, such as the CH_2F_2 and N_2 flow ratio, low-frequency source power (P_{LF}) and O_2 flow rate. It was found that the CH_2F_2/N_2 flow ratio was found to play a critical role in determining the process window for infinite SiON/EUV resist etch selectivity, due to the differences in change of the degree of polymerization on SiON and EUV resist. Control of N_2 flow ratio gave the possibility of obtaining the infinitely high etch selectivity by keeping the steady-state hydrofluorocarbon layer thickness thin on the SiON surface due to effective formation of HCN etch by-products and, in turn, in continuous SiON etching, while the hydrofluorocarbon layer is deposited on the EUV resist surface. On the other hand, CD size and LER tend to increase with increasing CH_2F_2/N_2 flow ratio.

Plasma Science and Technology
Room: A1 - Session PS1-ThM

Applications of Plasma-Surface Interactions
Moderator: L. Stafford, Université de Montréal, Canada

8:00am **PS1-ThM1 Coupled Ion, Photon and Electron Synergies in Plasma-Surface Interactions for Organic Materials**, ***D.B. Graves***, University of California at Berkeley

Recent experimental and simulation studies have revealed that plasma-organic surface chemistry can be strongly affected by synergistic interactions among ions, vacuum ultraviolet (VUV) photons and electrons at surfaces. In this talk, I summarize our recent studies of these synergies, focusing on various polymer and SiCOH low-k dielectric materials. When plasma and vacuum beam measurements, coupled with molecular dynamics (MD) simulations, are compared for various materials and various exposure conditions, certain patterns emerge. MD shows that (~ 100 eV) ion effects are restricted to several nm near the surface, but that their effects can depend strongly on the type of polymer and other species present. The synergistic effects of plasma-generated ions, photons and electrons can be understood in terms of a competition between bond-breaking scissioning reactions and bond-forming cross-linking and other reactions. The complexity of the results is due in part to the fact that these species have different depths of penetration, and that their bond breaking and bond forming reactions depend on the structure of the material. However, even greater complexity results from the fluence- or dose-dependent nature of electrons and ions: low dose result in scissioning and higher doses result in cross-linking. The effects of simultaneous exposure depend on both position relative to the surface and time. I illustrate these ideas with examples taken from PMMA-based 193 nm photoresists; poly-alpha methyl styrene (PaMS) and poly-four methyl styrene (P4MS); and ultra low k, nanoporous SiCOH. MD simulations and models of VUV photon penetration into polymers are used to interpret both plasma and vacuum beam experimental results.

8:20am **PS1-ThM2 Control of Photoresist Erosion in SiO_2 Plasma Etching in DC Augmented CCP Tools**, ***M. Wang***, Iowa State University, *M.J. Kushner*, University of Michigan

Polymer photoresists are commonly used for pattern transferring in plasma etching of sub-0.1 micron features in microelectronics fabrication. Degradation and erosion of the photoresist (PR) is a major issue in controlling feature profiles, especially for high aspect ratio (HAR) features where etch times are long. For example, during fluorine based plasma etching of SiO_2, erosion of the photoresist leads to bowing of the top of the profile as the etch proceeds. Multilayer masking is one approach to minimize these effects. By depositing a hard mask layer under the PR, the pattern is transferred to the hard mask layer before the PR is eroded away. Another promising strategy is to deposit a hard mask layer onto the PR surface during the process. This can be achieved in-situ by low energy ion bombardment of the PR surface to both promote cross-linking and produce dangling bonds, coincident to there being a flux of Si radicals. The resulting Si-C bonding provides a hard-mask like surface. Another is to promote fluorocarbon deposition on the PR mask to slow its erosion. These opportunities may be afforded by dc-augmented capacitively coupled plasmas (CCPs) in which the silicon covered dc electrode is sputtered. In this talk, we discuss scaling laws for profile and PR control derived from a computational investigation of a dc augmented single/dual frequency CCP reactor to generate an $Ar/C_4F_8/O_2$ plasma and fluxes of Si radicals by sputtering the dc electrode. Fluxes (energy and angle resolved) of ions, radicals and electrons are obtained from the Hybrid Plasma Equipment Model (HPEM) as a function of dc voltages, rf frequencies and rf bias powers. Profiles of features are then simulated by the Monte Carlo Feature Profile Model (MCFPM). Both multilayer mask and Si deposition strategies will be discussed. Etching selectivity between SiO_2 and mask material and feature profiles will be discussed as functions of Si fluxes, initial patterns and thickness of the photoresist.

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

8:40am **PS1-ThM3 Ultimate Top-down Processes for Future Nanoscale Devices - Novel Neutral Beam Process and Control of Atomic Layer Chemical Reaction**, ***S. Samukawa***, Tohoku University, Japan **INVITED**

For the past 30 years, plasma etching technology has led in the efforts to shrink the pattern size of ultralarge-scale integrated (ULSI) devices. However, inherent problems in the plasma etching, such as charge build-up and UV photon radiation, limit the etching performance for nanoscale devices. To overcome these problems and fabricate sub-10nm devices in practice, neutral-beam process has been proposed. In this paper, I introduce the ultimate etching processes using neutral-beam sources and discuss the fusion of top-down and bottom-up processing for future nanoscale devices. Neutral beams can perform atomically damage-free etching and surface modification of inorganic and organic materials. Namely, the neutral beam process can precisely control the atomic layer chemical reaction and defect generation. This technique is a promising candidate for the practical fabrication technology for future nanoscale devices.

9:20am **PS1-ThM5 Accurate Control of Ion Bombardment in an Expanding Thermal Plasmas**, ***P. Kudlacek***, *R.F. Rumphorst, A. Illiberi, M.C.M. van de Sanden*, Technical University Eindhoven, The Netherlands

Remote plasmas are extensively used in industry for both etching and deposition of materials. As ion bombardment has been found to be crucial for controlling deposited material properties or enhancing etch rate and anisotropy during ion induced etching, an additional bias voltage is often applied to the substrate to control the energy of the bombarding ions and/or enlarge their flux onto the substrate. Recently, a pulsed bias scheme became subject of increased interest as a promising technique to reach narrow, almost mono-energetic ion energy distribution (IED) when dielectric substrates are being processed, especially considering that the conventionally used radio frequency bias inherently leads to a bimodal IED. Moreover it offers an ultimate control of the ion flux onto the substrate by varying the duty cycle.

Experiments were run in a remote expanding thermal plasma (ETP) reactor, in Ar and Ar/H_2 gas mixture compositions. The substrate holder was negatively biased (up to -100V) by means of a home designed pulsed power supply operating with a frequency up to 200 kHz and a variable duty cycle. Ion energy distributions have been measured by means of a planar gridded retarding field energy analyzer.

Two pulsed biasing approaches will be presented (asymmetric rectangular pulses and modulated pulses with a linear voltage slope during the pulse) and their applicability is discussed on the basis of an intrinsic capacitance of the processed substrate-layer system. The substrate voltage and current waveforms were measured and mutual relations with the obtained ion energy distributions will be shown for both aforementioned cases. To demonstrate the IED control achieved, the effective carrier lifetime of n-type c-Si wafers, passivated by an a-Si:H thin film, as a function of the flux and energy of bombarding argon ions was determined. The ion energy and ion flux was independently varied and threshold ion bombardment characteristics leading to degradation of the effective lifetime will be presented.

9:40am **PS1-ThM6 Plasma Induced Modification of an Organic Photoconductor in an Electrophotographic System**, *K. Nauka*, ***S. Chang***, *H.-T. Ng*, Hewlett-Packard Company

The goal of this study was to elucidate structural and compositional modifications of an organic photoconductor after an extensive exposure to plasma discharge by a charging element within an electrophotographic system. An organic photoconductor, commonly found in a variety of applications ranging from simple copiers to advanced high-speed digital presses, is the key element of the modern electrophotographic printing system. It facilitates formation of the latent image resulting from the area-selective light discharge of uniformly distributed charges deposited on its surface by the plasma. Its undesirable modifications may adversely impact the print quality.

Modifications of the photoconductor's surface layer were investigated with the help of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR) and X-ray Photoelectron Spectroscopy (XPS). The experimental set-up was designed to simulate interactions between the plasma discharge and photoconductor occurring in a typical electrophotographic printing environment. Experiments were performed over an extended period of time corresponding to printing multiple pages. UV radiation and energetic particle bombardment originating from the plasma are the two major processes responsible for the photoconductor modifications. Therefore, further elucidation of the photoconductor modification phenomenon was obtained by employing the UV-only and the particle bombardment-only experimental conditions.

A long time exposure of the photoconductor to energetic neutral and charged species, and UV photons caused massive oxidation, substantial chemical bond breakage, and reformation of bonding configuration within a thin layer below the surface. This layer can be divided into two regions corresponding to the aforementioned photoconductor modification processes. The top region, having thickness of approximately 20nm - 30

nm, is formed primarily by the particle bombardment. It is heavily oxidized and its thickness is limited by the bombardment induced sputtering. Thicker region below is relatively free of oxygen and its molecular composition is distinctly different from the original photoconductor. It is primarily formed by UV-induced cracking of the benzene rings followed by reformation of the excited radicals into new molecular species. Thickness of this region corresponds to the UV penetration depth. The possibility of preventing the formation of a parasitic surface layer will be further discussed.

10:40am **PS1-ThM9 Control of Selectivity and Profile for HfO_2 Etching in BCl_3-Containing Plasmas**, ***K. Nakamura***, *Y. Ueda, H. Kiyokami, H. Tsuda, K. Eriguchi, K. Ono*, Kyoto University, Japan

Selective etching of high dielectric constant (high-*k*) films over the underlying Si (and/or SiO_2) is indispensable in the fabrication of high-*k* gate stacks. In practice, the selectivity is usually not so high, owing to highly volatile halogen compounds of Si, and also to strong metal-oxygen bonds of high-*k* dielectrics and less volatile metal-halogen compounds. Profile control is also indispensable during etching of high-*k*: anisotropic profiles are required for high-*k*, and also profiles of gate electrodes on high-*k* are required to remain unchanged. This paper presents the control of selectivity and profile for high-*k* HfO_2 etching under low ion-energy conditions in BCl_3-containing plasmas, with emphasis being placed on a better understanding of the etching mechanisms concerned. Experiments were performed in both electron cyclotron resonance (ECR) and inductively coupled (ICP) plasmas, by varying pressure, additive concentration of O_2, Cl_2, and Ar, rf bias power, and also substrate temperature. Samples for etching were blanket HfO_2 and TaN films, and separate Si and SiO_2 substrates were also employed for reference. Samples of TaN/HfO_2 stack as well as separate HfO_2 and TaN masked with line-and-space patterns were also employed to examine the etched profile. We examined substrate surfaces by x-ray photoelectron spectroscopy, and investigated reactant and product species in the plasma during etching by optical emission spectroscopy and quadrupole mass spectrometry. A transition from deposition to etching regimes was found to be caused on all substrate surfaces, by varying pressure, by using additives such as O_2 and Cl_2, and by increasing rf bias power. In practice, surface inhibitor deposition was less significant for HfO_2 than for Si, SiO_2, and TaN; and the threshold bias power or ion energy for HfO_2 etching was in the range 10-20 eV, while the threshold was more than 20 eV for the other. A difference in pressure, additive concentration, and bias power for the transition between HfO_2 and Si (and/or SiO_2) gave rise to high or infinite selectivity of high-*k* over Si (and/or SiO_2), together with vertical high-*k* profiles. The difference for the transition between HfO_2 and TaN also gave no significant distortion of TaN profiles during HfO_2 etching, owing to passivation layers deposited on TaN sidewalls. Plasma and surface diagnostics indicated that inhibitor species for deposition are primarily boron-chloride polymers produced in the plasma, whose concentration largely depends on pressure, additive concentration, and plasma reactor (ECR and ICP), which in turn leads to a marked difference in etching characteristics.

11:00am **PS1-ThM10 Etching Mechanisms of FeCo Magnetic Films by Chemically Reactive Energetic Ion Injections**, ***K. Karahashi***, *T. Ito, Y. Matsumoto, S. Hamaguchi*, Osaka University, Japan

Reactive ion etching (RIE) has been widely used for semiconductor micro fabrication processes. Recently magnetic thin films have also become materials of choice for some specific microelectronics applications such as magnetic random access memory (MRAM) and read/write heads for magnetic data storage. For micro fabrication processes of magnetic films, Ar ion milling seems to be almost the only etching technique in the current manufacturing processes. However, capabilities of Ar ion milling for anisotropic and selective etching of magnetic films are severely limited and therefore new technologies of reactive ion etching for magnetic films are now seriously sought. In this study, we have focused on etching processes of FeCo alloy thin films and examined their surface reactions caused by energetic Cl+ ion beam injections. More specifically we have measured desorbed products and etching yields (i.e., sputtering yields) of the sample, using a mass-selected ion beam system. The ion beam system can inject mono-energetic single-species ions (i.e., Cl+ or Ar ions in this study) to the sample (i.e., FeCo, Fe, or Co thin film) surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with a quadrupole mass spectrometer (QMS), a temperature programmed desorption (TPD) system, and an X-ray photoelectron spectroscopy (XPS). The QMS is used for the detection of desorbed products during the ion beam injections and XPS is used for in-situ chemical analyses of irradiated surfaces. The Cl+ ion beams used in this study are in the range of 250-1000eV. The etching yields are determined from measured depth profiles of irradiated surfaces and ion fluxes. It has been found that the etching yields of FeCo and Fe films by Cl+ ion injections below 300 eV are smaller than those of Co films under the same conditions. It has been also found that iron chlorides (FeClx) are formed on Fe surfaces under Cl+ ion injections and their amounts increase with the increasing Cl+ ion dose. These results indicate that the reduction of etching rate of FeCo below 500eV is caused by the formation of FeClx on the surface. TPD of volatile materials from Cl+ injected Fe surfaces has shown that FeClx desorbs when the surface temperature is above 600K. This suggests that the control of substrate temperature is crucial for Cl-based reactive ion etching of FeCo. We have also compared these results with physical sputtering characteristics of FeCo films by energetic Ar injections.

11:20am **PS1-ThM11 Characterizing the Effects of Etch-Induced Material Modification on the Crystallization Properties of Nitrogen Doped $Ge_2Sb_2Te_5$**, *E.A. Joseph, S. Raoux, J.L. Jordan-Sweet,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, *D. Miller, H.-Y. Cheng,* IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr, *A. Schrott, C.-F. Chen, R.K. Dasaka,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, *R.M. Shelby,* IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr, *Y. Zhang,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr, ***J.S. Washington***, *M.A. Paesler, G. Lucovsky*, North Carolina State Univ.

Chalcogenide-based phase change memory devices have recently garnered significant interest due to their potential scalability beyond that of conventional DRAM and Flash memory technologies.[1] Due to the stringent demands imposed by the scaling roadmap, it is becoming increasingly important to understand the effects of processing on the crystallization properties of the material since it is known that there is an etch-induced material modification layer resulting from patterning.[2] In this work, we examine chemical and structural effects of processing on the crystallization properties of nitrogen doped Ge2Sb2Te5 using X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), time resolved laser reflectivity and time resolved X-ray diffraction (XRD). The laser reflectivity results indicate that upon exposure to various etch and ash chemistries the (re)crystallization speed is significantly reduced. Time resolved XRD data further show that the transition temperature from the rocksalt to the hexagonal phase is increased from 400 ºC to ~ 500 ºC. From depth profiled XPS and XAS measurements, we attribute this increase in crystallization time (and increase in transition temperature) to the selective removal and/or oxidization of numerous elemental species (N, Ge, Sb, Te) which alters the local bonding environment and which may result in the formation of additional phases. The relevance of these effects and their ability to potentially alter device performance will also be discussed.

[1] Y.C. Chen, C.T. Rettner, S. Raoux *et al.*, IEDM Tech. Dig., p. S30P3, 2006.

[2] E. A. Joseph, T. D. Happ, S.-H. Chen, S. Raoux, et al., Symp. VLSI-Technology Systems and Applications, 2008. pg 142-143, 2008

11:40am **PS1-ThM12 Surface Properties of Plasma Treated Metal Oxides**, ***K. Trevino***, *E.R. Fisher*, Colorado State University

Metal oxides are used for various applications including polymer adhesion, anticorrosive coatings, and catalysis. Plasma treatments have proven useful in tailoring the properties of such surfaces due to their ease of use and environmental friendliness. However, the interfacial interactions that give rise to changes in surface charge and acid/base character are poorly understood. Measurement of these properties, along with surface characterization, allows for a clearer understanding of the important chemical processes. Of particular concern is the permanency of the surface treatment, which is expected to depend on plasma type, plasma conditions, substrate, and the position of the substrate in the plasma. In this work, we have separately treated SiOxNy surfaces with three non-polymerizing gases (Ar, H_2O, and NH_3) and monitored surface properties as a function of plasma parameters and substrate position for a period of thirty days. Surface charge and acid/base character were measured by determination of the isoelectric point (IEP) from contact angle titration data; surface composition and morphology were also taken and analyzed by XPS and SEM. Ar-plasma treatments yielded initial IEP values of ~7, however these values are not stable over time. In contrast, IEP values for H_2O plasma treatments also increased (compared to an untreated substrate) to ~6, but stay relatively stable with age. Compositional data reveal information about the effectiveness of the treatments, and IEP data highlight the similarities and differences between the plasma systems. Results from additional metal oxides and polymer surfaces will also be presented and comparisons between systems will be made.

Plasma Science and Technology
Room: B2 - Session PS2-ThM

Plasma Sources
Moderator: J.-P. Booth, CNRS/Ecole Polytechnique, France

8:00am **PS2-ThM1 Power Dynamics in Low Pressure Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *K. Bera, L. Dorf, K. Collins*, Applied Materials, Inc.

As feature sizes shrink and feature aspect ratios increase in advanced microelectronics devices, critical dielectric etching processes in capacitively coupled plasmas (CCP) are generally transitioning towards lower gas pressures (< 30 mTorr). Long electron mean free path and large bias voltages in this regime means that kinetic effects play an important role in the power dynamics in these low pressure plasma discharges. A coupled one-dimensional particle-in-cell (PIC) and fluid model is used to understand power dynamics in low pressure CCP discharges in this investigation. Our PIC model for charged species is based on the well-established computational techniques developed by Birdsall and colleagues (C. K. Birdsall and A. B. Langdon, *Plasma Physics via Computer Simulation*, IOP Publishing, Bristol, 1991) and includes a Monte Carlo based model for charged species collisions. Since multiple neutral species are present in plasmas of typical etching gases, the PIC model is coupled to a fluid model for neutral species that takes into account species transport in the plasma bulk, chemical reactions, and surface processes. The PIC + fluid model is applied to understanding power dynamics in a variety of etching-relevant single and dual frequency plasmas including Ar, O_2, and CF_4. Substantial fraction of applied power is consumed by the ions in the sheaths, which is dissipated at the electrodes. In Ar, electrons primarily gain energy at the sheath edge during sheath expansion, which results in highly energetic electrons. These energetic electrons stream through the plasma towards the opposite electrode, causing excitation, dissociation and ionization in their path. At low pressures (< 50 mTorr), these energetic electrons are able to reach the opposite sheath and lose some their energy while decelerating in the sheath. This behavior is consistent with the fact that plasma density is lower at lower pressure in the 5 – 50 mT range. The situation becomes more complicated in molecular gases due to electron collision processes with low threshold energies. Secondary electrons play an important role in sustaining the plasma at low frequencies (< 30 MHz), but sheath heating of electrons is sufficient for plasma sustenance at higher frequencies (> 60 MHz). Simulation results will be compared to experimentally measured ion densities.

8:20am **PS2-ThM2 Ballistic Electrons and Resulting EED*f* in a DC+RF Hybrid CCP Reactor**, ***L. Xu***, *L. Chen, M. Funk*, Tokyo Electron America

The DC+RF Hybrid is a capacitively coupled plasma (CCP) etcher with RF applied to the wafer electrode and a high-negative DC voltage on the opposite electrode 3cm away. Ion-secondary-electrons from the DC electrode are accelerated by the DC-sheath into the plasma as ballistic electrons. Gridded energy analyzers are placed behind the RF electrode for EED*f* measurements. Experiment's pressure-range varies from 30 mTorr to 70 mTorr with DC-voltage up to –1kV. EED*f* reveals, (1) Maxwellian bulk, (2) ballistic electrons with energy corresponding to the applied DC-voltage, (3) a continuum from Maxwellian to the ballistic electron peak, (4) middle-energy electrons with distinct energy-peak. Measured EED*f* qualitatively agree with PIC numerical experiment. The energy of the distinct middle-energy peak seems to depend on the sheath thickness and varies from ~ 40eV to 300eV. While ballistic electrons' finite collisions contribute to the continuum, other non-negligible channel such as Landau-damped e^--beam plasma waves, should be considered. The distinct middle-energy peak could result from Landau damping of a strong plasma wave of a specific wave number. The energy range of middle-energy peak is favorable in sustaining ionization, rendering the necessity of heating the Maxwellian bulk for a similar level of ionization.

8:40am **PS2-ThM3 Simulation of 450 mm Dual Freqeuncy Capacitively Coupled Plasma Tools: Conventional and Segmented Electrodes**, ***Y. Yang****, Iowa State University, *M.J. Kushner*, University of Michigan

Wafer diameters will soon transition from 300 mm to 450 mm at a time when excitation frequencies for capacitively coupled plasmas (CCPs) are increasing to 200 MHz or higher. Already for 300 mm tools, there is evidence that wave effects (i.e., propagation, constructive and destructive interference) affect the processing uniformity. The increase to 450 mm is likely to exacerbate these affects, perhaps requiring non-traditional tool designs. This is particularly important in dual frequency (DF) CCP tools in which there are potential interactions between frequencies. In this talk, we discuss results from a 2-dimensional modeling study of the plasma properties in 450 mm DF-CCP tools. To resolve wave and electrostatic effects, a full-wave Maxwell equation solver in the Hybrid Plasma Equipment Model is employed. To capture the high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. A Monte Carlo simulation is also used to predict ion energy distributions as a function of radius on the substrate. Results will be discussed for plasma properties in DF-CCPs for low frequencies of ≤ 10 MHz and high frequencies up to 200 MHz, and gas pressures of < 10s mTorr. Segmented electrodes will be discussed as a means to suppress wave effects by making the electrical distance between the electrode feeds and the sheath edges as uniform as possible. The effects of tuning the lengths of the segments and the positions of rf feeds on plasma uniformity will be discussed.

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

9:00am **PS2-ThM4 A Scalable, VHF/UHF Compatible, Capacitively Coupled Plasma Source for Processing Large-Area Substrates at High Frequencies**, ***A.R. Ellingboe***, *D. O'Farrell, C. Gaman*, Dublin City University, Ireland, *F. Green, N. O'Hara, T. Michna*, Phive Plasma Technologies, Ireland

A recent trend in plasma etching and plasma enhanced CVD has been the increase in rf frequency used to sustain the plasma. For capacitively coupled plasma sources, increasing the rf frequency increases the fraction of power coupled into the electrons in comparison to ion energy gained in the sheath. The concept of 'high-frequency chemistry' is discussed, and some evidence that systems operated at hundreds of Megahertz have different electron kinetics have been presented (Samukawa, etal, J. Vac. Sci. Technol. A 17(5), Sep/Oct 1999, and D.O'Farrell, this conference).

However, the present trend to increase rf frequency is incompatible with increases in wafer size to 450mm and beyond.

No where is the evidence more clear than in PECVD of amorphous and microcrystalline Silicon for the photo-active layer in thin-film photovoltaic devices. Growth rates for these layers, while maintaining the necessary mechanical and electrical properties, can increase with increasing rf frequency, and in some cases yield superior film properties at the higher deposition rates (P.G. Hugger, etal, MRS 2008). However, in this industry substrate sizes are very large, exceeding 1m characteristic lengths, which puts substantial limits for a conventional plasma diode topology on using frequency as a control vector to increase deposition rate, thus increasing factory through-put and decreasing cost.

In this talk we will introduce a novel plasma source topology that enables increased rf frequencies on arbitrary size plasma source without causing wavelength effects. The concept is to segment the powered electrode into discrete tiles; For example as a checkerboard. Adjacent tiles can be powered out of phase with each other. In this way the displacement current coupled by one electrode is balance by and equal and opposite current of the adjacent electrode. Thus zero net current is coupled into the plasma, zero net current is coupled through the sheath above the substrate, and no wavelength effects occur even for substrates large in comparison to the rf wavelength.

Highlights of recent results in the operation and application of the plasma source to PECVD of silicon will be presented.

9:20am **PS2-ThM5 Characteristics of Ferrite Enhanced Internal Linear Antenna for Large Area (2750mm x 2350mm) Inductively Coupled Plasma Source**, ***J.H. Lim***, *K.N. Kim, G.H. Gweon, S.P. Hong, G.Y. Yeom*, Sungkyunkwan University, Korea

Inductively coupled plasmas sources (ICPs) have been applied to a variety of plasma processing including flat panel display processing (FPD) and semiconductor processing. Especially, for the FPD applications, to increase the inductive coupling to the plasma, internal-type antennas have been more intensively investigated.

In this study, the plasma characteristics of an internal-type linear ICP source having the size of 2750mm χ 2350mm installed with a Ni-Zn ferrite module was investigated. Especially, the effect of the Ni-Zn ferrite and different driving frequency of 2MHz and 13.56MHz on the plasma characteristics and electrical characteristics of the plasma source was investigated.

The results showed that, by the magnetic field enhancement using the ferrite, the operation of the antenna at 2MHz showed higher power transfer efficiency, lower antenna impedance, and lower rf rms voltage compared to that operated at 13.56MHz without the ferrite. For the ferrite enhanced ICP source operated at 7kW of 2MHz rf power, high density plasmas on the

* PSTD Coburn-Winters Student Award Finalist

order of 2.0 x 10^{11}cm^{-3} could be obtained with 15mTorr Ar which was about two higher than that obtained for the source operated at 13.56MHz. When photoresist etch uniformity was measured by etching the phtoresist using 40mTorr Ar/O_2(7:3) mixture for the operation at 2MHz with the ferrite module, the etch uniformity of about 11% could be obtained.

9:40am **PS2-ThM6 Large-Scaled ECR Line Plasma Production by Microwave in a Narrowed Rectangular Waveguide**, ***H. Shindo***, *Y. Kimura,* Tokai University, Japan*, T. Hirao*, Kochi Institute of Technology, Japan

Long line-shaped plasmas are inevitable in material processing in manufacturing industries, such as solar cell film CVD, flat panel displays (FPDs), and various surface modification of large-area thin films. In this work, a newly proposed method of large-scaled line plasma production is studied. In particular a long line ECR (Electron Cyclotron Resonance) plasma production is examined. In this method, microwave power of frequency of 2.45 GHz in a narrowed and flattened rectangular waveguide is employed to produce a long uniform ECR line 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 line high density plasma with a great uniformity.

The narrowed rectangular wave-guide of 1.0 and 2.0 m in length and 5mm in height were prepared and the width of the waveguide is 62 mm which is very closed to the cut-off condition. The waveguide has a long slot on the top surface to launch the micro-wave into the discharge plasma chamber of 1.0 and 2.0 m in length. At the end of wave guide, a short plunger was quipped to adjust the phase of the standing microwave, hence the uniformity of the plasma thus produced. The magnetic field, which is generated by NdFeB magnet of 20 mm in thickness and 50 mm in width, is applied to plasma to produce the resonance field of 875 Gauss at the position of 10mm below the slot antenna. The plasmas of Ar at the pressures of 0.5 to 5Torr were produced by employing an extremely long microwave wavelength. The plasma thus produced was three-dimensionally measured by a Langmuir probe.

The electron density in the plasma thus produced showed a very high value, as high as 10^{12} cm^{-3} at the pressure of 0.5 Torr. In particular the cross sectional profile of the electron density showed a strong magnetic filed dependence and it becomes highest at the ECR resonance point, one order higher than in non-resonance region, indicating that the plasma production is due to the electron cyclotron resonance. The axial profile of electron density is quite good and the plasma uniformity was within 5 % in the entire plasma, indicating that the ECR line plasma is realized. It was also found that the profile of electron density was adjustable by the short plunger. To be specific, the electron density measured at a fixed Z position showed a standing wave-like profile, indicating the short plunger has a function of phase-shifter as expected. Thus we conclude that the present method of large-scaled ECR line plasma production is quite advantageous for large area processing.

10:40am **PS2-ThM9 PIC Simulations and Probe Measurements of the EEDF in a Microwave Surface-Wave Plasma Source***, **R.V. Bravenec**,* Fourth State Research, under contract to Tokyo Electron America, Inc.*, J.P. Zhao, L. Chen, M. Funk,* Tokyo Electron America, Inc.*, C.Z. Tian, K. Ishibashi, T. Nozawa*, Tokyo Electron Technology Development Institute, Japan

Microwave surface-wave plasma sources for wafer etching or deposition are promising alternatives to capacitively- or inductively-coupled sources. Unlike the latter, the source and wafer are decoupled, such that the wafer may be independently biased without affecting the source. Furthermore, microwave surface-wave sources are known to produce relatively dense, quiescent, low-temperature plasmas near the wafer surface, thereby minimizing wafer damage. Our device consists of an RLSA (radial line slot antenna) which transmits 2.45 GHz microwaves into a large quartz resonator disk which then couples to the plasma. We compare 2-D PIC (particle-in-cell) simulations from the VORPAL code[1] with Langmuir probe measurements[2] of the EEDF (electron energy distribution function) of the plasma. The simulations, a continuation of earlier work,[3] include ionization using a Monte-Carlo model with an energy-dependent cross section. Secondary emission from the quartz surface is modeled with energy and incident-angle dependent yield and produces a specific energy spectrum of outgoing particles. Fitting of the probe I-V curves employs a novel method of assuming from the outset two Maxwellian distributions plus a drifting Maxwellian to model a beam component. This method, unlike fitting the curves to polynomials or such, aids in interpretation of the results. We find that the EEDF near the resonator disk is typically dominated by the beam component, transitions to two Maxwellians away from the disk, then thermalizes to a single cold Maxwellian near the wafer surface. Simulations and data for various plasma densities and gas pressures will be presented.

[1]C. Nieter and J. R. Cary, J. Comp. Phys. **196**, 448 (2004).

[2]J. P. Zhao et al., poster at this conference

[3]R. V. Bravenec et al., poster at Gaseous Electronics Conference, Dallas, Oct., 2008.

(Research funded by Tokyo Electron Technology Development Institute. The authors also acknowledge the contributions of C. Roark, D. Smithe, and P. Stolz of Tech-X Corp.)

11:00am **PS2-ThM10 Characterization of an Expanding Chlorine Plasma Produced by an Electromagnetic Surface-Wave***, **O. Boudreault**, S. Mattei,* Université de Montréal, Canada*, R. Khare,* University of Houston*, L. Stafford,* Université de Montréal, Canada*, V.M. Donnelly*, University of Houston

Plasmas produced by propagating surface waves have attracted attention because of their long and stable plasma columns without accompanying guiding structures. This is because the electric field supporting the discharge is provided by a traveling wave that carries the power away from the applicator, guided by the plasma column and the dielectric tube enclosing it. In long, narrow plasmas the wave-to-plasma power transfer is usually assumed to occur locally such that the axial density profile is determined by the wave attenuation coefficient. As a result the electron density, n_e, decreases in a quasi-linear manner along the plasma column in the direction of the wave propagation down to the critical density for surface wave propagation where the plasma decays abruptly (= expansion region) . At low pressures, however, the plasma tends to expand well beyond this critical point such that the description of the axial density distribution in terms of the local approximation is no longer valid. We investigated the influence of gas pressure on the spatial structure of a high-density chlorine plasma produced in a 6 mm, inside diameter, quartz tube by a propagating 2450 MHz surface wave. The axial variation of the electron density was determined from the spatial phase characteristics of the wave and the 828.0 nm emission line of Xe inserted as a tracer. As expected, n_e decreased linearly with axial position from the wave launcher, except in an expansion region near the end of the plasma column where the decrease of n_e was more abrupt. The thickness of this expansion region decreased with increasing pressure, going from about 8 cm at 5 mTorr to less than 1 cm at 100 mTorr. The Cl_2 percent dissociation obtained from the calibrated Cl_2(306 nm)-to-Xe emission ratio remained fairly constant except in the expansion region where it decreased sharply. For example, at 5 mTorr, the Cl_2 percent dissociation was 95 % near the wave launcher and 15 % at 2 cm from the end of the plasma column. While the expansion region showed a decrease in the electron density and Cl_2 percent dissociation, no noticeable change in the electron energy distribution function (EEDF) was observed. For all pressures and axial positions, the EEDF determined by trace-rare-gas-optical-emission-spectroscopy remained Maxwellian. The electron temperature (T_e) was fairly independent of the axial position, going from ~12 eV at 5 mTorr to ~2 eV at 100 mTorr. The high T_e values are due to a combination of high gas temperatures (T_g = 463 K at 5 mTorr and 635 K at 100 mTorr, measured by N_2 C->B emission rotational spectra) and small tube bore (0.6 cm), and are in good agreement with a global model.

11:20am **PS2-ThM11 Vacuum Ultraviolet Plasma Emission in a Capacitively-Coupled Dielectric Etch Reactor***, **E.A. Hudson**, M. Moravej, M. Block, S. Sirard, D. Wei, K. Takeshita,* Lam Research Corp.*, B. Jinnai, S. Samukawa*, Tohoku University, Japan

Plasma optical emission in the visible and ultraviolet (UV) ranges is widely used to characterize the properties of thin-film processing plasmas. Emission in the vacuum ultraviolet (VUV) range is less commonly detected due to the challenges of eliminating air from the optical path. However the interaction of VUV radiation with the substrate may be important in plasma processing, particularly for device damage and for the modification of sensitive materials such as low-k dielectrics and 193nm photoresist. To improve the understanding of these mechanisms, a windowless optical system was incorporated onto a commercial capacitively-coupled confined-plasma dielectric etch reactor. VUV and UV emission spectra in the 40 – 230nm range were measured for a range of plasma conditions, including simple single-gas plasmas and more complex etching plasmas. The spectra showed a strong dependence on gas chemistry, due to the characteristic emission lines associated with the plasma atomic and molecular composition. More importantly, the frequency of plasma electrical excitation was found to influence the VUV spectra. Correlations were observed between plasma emission in specific wavelength ranges and process-induced low-k dielectric damage.

11:40am **PS2-ThM12 Damage-Free, Uniform and High-Target-Utilization Novel Magnetron Sputtering Plasma Source by Rotating Helical Magnet**, ***T. Goto***, Tohoku University, Japan, *N. Seki, T. Matsuoka,* Tokyo Electron Technology Development Institute, Inc., Japan, *T. Ohmi*, Tohoku University, Japan

Novel magnetron sputtering equipment, called rotation magnet sputtering (ROT-MS), is being developed to overcome various disadvantages of current magnetron sputtering equipment. Disadvantages include:(1) very low target utilization of less than 20%, (2) difficulty in obtaining uniform deposition on the substrate, and (3) charge-up damages and ion-bombardment-induced damages resulting from very high electron temperature and that the substrate is set at the plasma-excitation region. In ROT-MS, a number of moving high-density plasma loops are excited on the long rectangular flat target surface by rotating helical magnets, and the deposition is performed by passing the substrate through this deposition region, resulting in very high target utilization with uniform target erosion and uniform deposition on the substrate due to time-averaging effect. T his excellent performance can be principally maintained even as equipment size increases for very large-substrate deposition. Plasma characteristics and deposition performances were investigated using ROT-MS equipment for both 8-inch wafer and 200-mm-square substrate. Deposition uniformity on 8-inch wafers for pure Al deposition results in that the film-thickness uniformity (defined by standard deviation divided by average thickness) is 0.5～2.5% in the wide pressure range from 0.33 to 5.3 Pa for the cases without any optimization of slit width configuration. The target utilization is estimated to be 59.7% from the measurement of the target erosion distribution. It is found that the target erosion distribution experimentally observed agrees well with the theoretical calculation. We have calculated target utilization for various helical magnet configurations, and revealed that very high target utilization larger than 90% is feasible. Detailed ion current distributions at the substrate were measured by measuring ion saturation currents flowing to the multipoint probes set at the stage (in this measurement, the helical magnet is not rotating). The results show that the distribution is uniform within the slit area for the rf-excited plasma case with the order of 1 mA/cm^2, while the distribution of the magnetic filed loop pattern is observed with the order of 0.1 mA/cm^2 for the dc-excited case. Because strong horizontal magnetic fields (>0.05 T) are produced within a very limited region just at the target surface, very low electron-temperature plasmas (< 2.5 eV for Ar plasma, and < 1 eV for direct-current-excited Xe plasma) are excited at the very limited region adjacent to the target surface for charge-up damage-free and ion-bombardment-induced damage-free processes.

Plasma Science and Technology
Room: A1 - Session PS1-ThA

Fundamentals of Plasma-Surface Interactions II
Moderator: D.J. Economou, University of Houston

2:00pm **PS1-ThA1 Negative Ion Surface Production in Low Pressure Plasma**, ***G. Cartry***, *L. Schiesko, J.M. Layet, M. Carrere*, PIIM, Aix - Marseille Université - CNRS, France **INVITED**

Negative ions in plasmas play a main role in the discharge kinetics. For instance they may be at the origin of plasma instability [1], or may be responsible for coalescence in the primary state of dust formation [2]. Plasma based negative ion sources can have many applications. They may be used to reduce surface charge during plasma etching and in the context of controlled fusion research, they are used to generate neutral beams to heat fusion plasma. Therefore controlling negative ion production and loss in plasmas is of primary interest in many research fields. Efficient negative ion sources use caesium deposited on surfaces to increase negative ion production. Indeed, due to its property of reducing the work function, caesium leads to a high negative ion surface production yield. Negative ions are also produced in plasma bulk through electron attachment on molecules. Up to now most of works focused on plasma bulk production and on caesiated-surface production. Few works deal with caesium free surface production while almost all low pressure plasma sources are running without caesium. The aim of the present paper is to study caesium free negative ion surface production in low pressure plasmas.

Our first study is concerned with H2/D2 plasmas and graphite material for fusion applications [3]. However, results obtained here can be extended to low pressure plasma sources used in microelectronic industry for instance, since carbon containing materials are often in interaction with H2 plasmas or even more electronegative plasmas such as oxygen, fluorine or chlorine containing plasmas.

We use a helicon reactor whether in capacitive or inductive mode. A mass spectrometer is placed in the diffusion chamber of the helicon reactor and faces a one square centimetre graphite sample. The sample is negatively biased with respect to the plasma. Positive ions (H+, H2+, H3+) bombards it and negative ions formed (H-) upon bombardment are repelled from the surface toward the plasma. Under low pressure considered here, they reach without any collision the mass spectrometer where they are analysed according to their energy. Study of negatve Ion Distribution Function (IDF) provides information on surface production mechanisms. In this talk we will discuss IDFs measurements, describe how we identify surface production mechanisms, show negative ion surface production yield dependency with positive ion flux and energy, and compare H2 and D2 plasmas.

The authors acknowledge ANR (project ITER-NIS BLAN08-2_310122)

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[2] Bouchoule A et al 1996 Pure Appl. Chem.68 1121

[3] L Schiesko et al Pl. S. Sci. Tech.17 (2008) 035023

2:40pm **PS1-ThA3 Amorphous Hydrogenated Carbon Etching with a Low Energetic Plasma Jet**, ***T.A.R. Hansen***, *J.W. Weber, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, The Netherlands

Structures in the chip industry are approaching the 32 nm half pitch, which requires radiation in the VUV and EUV range. Cracking of hydrocarbon impurities in the vacuum by the radiation causes C growth on the VUV and EUV optics. Each nm of deposited carbon reduces the reflectivity of the optics by 1%. Fast removal of these contamination layers without damage to the underlying optics is essential for the next generation of lithography devices.

Etching with a low energetic plasma jet can be used to selectively remove coatings such as hydrogenated amorphous carbon (*a*-C:H) without damage to the underlying structure. Real time, *in situ* spectroscopic ellipsometry measurements indicate that the highest etch rates are obtained for an Ar/H_2 plasma, rather than for a pure Ar or H_2 plasma.

Even though the etch rate of *a*-C:H thin films is dependent on both temperature and roughness, the highest roughness in absolute values is attained by the plasma with the lowest etch rate. At low temperatures, the etch rate deviates from an Arrhenius relation, while the activation energy is similar for both the H_2 and Ar/H_2 plasma at higher temperatures.

The two orders of magnitude higher etch rate for the Ar/H_2 plasma is due to chemical sputtering, which is a synergistic effect between atomic H and Ar^+ ions with an ion energy below the threshold of 58 eV for physical sputtering. Chemical sputtering has been observed by Hopf et al. for energies above 20 eV and an H to Ar^+ flux ratio over 100 [1]. In our plasma, however, the Ar^+ ion energy is only a few eV's and the estimated H to Ar^+ ratio is lower than 5.

The etch products, released from the surface, consist mainly of CH_4 and C_2H_y, as shown by residual gas analysis. Time resolved optical emission spectra of the Ar/H_2 plasma, from a few mm's in front of an *a*-C:H sample, indicates also the presence of C_2 and CH radicals. The CH radical is formed in the plasma phase through charge transfer between Ar^+ ions and these larger hydrocarbons, and dissociative recombination. Similar plasma chemical processes occur during the remote plasma deposition of *a*-C:H films. However, in contrast with deposition, the CH rotational temperature shows an overpopulation in the higher excited states, indicating that the (internal state of the) parent molecule is different for an etch plasma than for a deposition plasma.

Spatially resolved optical emission measurements are Abel inverted, by means of the numerical Barr method. While there is some CH production throughout the entire plasma jet, the highest CH production occurs in front of the *a*-C:H sample.

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3:00pm **PS1-ThA4 Investigation of Fluorocarbon PECVD During Processing of Si and ZrO_2 Surfaces**, ***M. Cuddy***, *E.R. Fisher*, Colorado State University

Films deposited from fluorocarbon (FC) plasmas exhibit low dielectric constants desirable for interlayers in ultra-large scale integrated circuits (ULSIs). The processing of ULSIs has involved the use of small monomer (CF_4, C_2F_6) FC precursors as an avenue for plasma-enhanced chemical vapor deposition (PECVD). To gain a broader understanding of both the FC plasma system and plasma-surface interactions, we have explored gas phase diagnostics and species-surface reactivity under varying plasma parameters. This presentation will reflect upon data obtained from optical emission spectroscopy (OES) concerning the role of excited state species present in FC plasmas. OES data show that during FC plasma treatment of Si and ZrO_2 wafers, CF_2* concentrations increase independent of feed gas and substrate type. The films deposited from such treatments do, indeed, consist of FC moieties and thus plasma-surface interactions are clearly influential in the overall process. We have studied the interaction of FC plasma species at the interface of depositing films using the imaging of radicals interacting with surfaces (IRIS) technique. IRIS data show that scatter probabilities for the CF_2 radical are greater than unity, indicating that CF_2 is produced from films *at the surface* during FC plasma processing of silicon. Furthermore, we have used quadrupole mass spectrometry to investigate mean ion energies of CF_2^+ in FC plasmas and have discovered that ion energies increase with increasing applied rf power. We have previously demonstrated that IRIS scatter coefficients for CF_2 produced from larger precursors (C_3F_8 and C_4F_8) correlate directly with ion energy. Thus, we will explore the role of this radical during processing of Si and ZrO_2 with small FC precursors as monitored by IRIS studies and compare these results with the respective ion energies for CF_2^+ in these systems.

3:40pm **PS1-ThA6 Studies of Chlorine-Oxygen Plasmas and Evidence for Heterogeneous Formation of ClO and ClO_2**, ***V.M. Donnelly***, *J. Guha*, University of Houston

Plasma and surface diagnostics of Cl_2/O_2 mixed-gas inductively coupled plasmas are reported. Using trace rare gas optical emission spectroscopy (TRG-OES) and Langmuir probe analysis, electron temperatures (T_e) and number densities for Cl atoms (n_{Cl}), electrons (n_e), and positive ions were measured as a function of percent O_2 in the feed gas and position in the plasma chamber. Adsorbates on, and products desorbing from a rotating anodized aluminum substrate exposed to the plasma were detected with an Auger electron spectrometer and a quadrupole mass spectrometer. T_e and n_e increased with increasing percent O_2 in the plasma, while n_{Cl} fell off with O_2 addition in a manner reflecting simple dilution. Cl atom recombination probabilities (γ_{Cl}) were measured and were found to be a nearly constant 0.036±0.007 over the range of Cl_2/O_2 mixing ratios and Cl coverage. Large yields of ClO and ClO_2 were found to desorb from the surface during exposure to the plasma, ascribed predominantly to Langmuir-Hinshelwood reactions between adsorbed O and Cl. In addition, the transient surface composition of an anodized aluminum surface was determined as the gas was switched from Cl_2 to O_2 and vice versa. When the surface was first conditioned in an O_2 plasma and then exposed to Cl_2 plasmas, a rapid uptake of Cl was found in the first tens of seconds, followed by a slow approach to a steady state value within ~5 minutes of plasma exposure. Conversely, when the surface was exposed to a Cl_2 plasma for a long time and then switched to an O_2 plasma, the anodized aluminum surface

underwent a rapid de-chlorination in the first few seconds and then a slow approach to steady state over ~3 minutes. The buildup and decay of Cl coverage is well described by a stretched exponential function, reflecting a range of binding sites for Cl. Throughout these treatments, the coverages of Si (from erosion of the quartz discharge tube) and O was nearly constant.

4:00pm **PS1-ThA7 Etching of Silicon and Silicon Oxide in a Pulsed Inductively Coupled Plasma with Chlorine**, ***C. Petit-Etienne***, LTM/UJF, France, *L. Vallier, E. Pargon, O. Joubert*, LTM/CNRS, France

For the next technological generations of integrated circuits, the traditional challenges faced by etch plasmas (profile control, selectivity, critical dimensions, uniformity, defects, ...) become more and more difficult, intensified by the use of new materials, the limitations of lithography, and the recent introduction of new device structures and integration schemes. Chemical plasma composition can be changed by modifying the gas mixture, ion flux can be partly controlled by source power, and ion energy can be chosen thanks to the bias voltage applied to the substrate. However, these control parameters are not always sufficient to reach all required etching characteristics and new control parameters are needed. Pulsing the plasma source power or the substrate bias offers new operating parameters (pulse frequency, duty cycle). The main advantages of a pulsed etching process are the improvement of etch selectivity and the reduction of charge-up damages and defects by reducing the electron activity and controlling the dissociation of radicals in the plasma.

Studies are being conducted on the etching characteristics of silicon and silicon dioxide in a 300 mm industrial inductively coupled plasma etching chamber having pulsed plasma discharge capability from Applied Materials. The reactor has been modified to be connected to an Angle-Resolved X Ray Photoelectron spectroscopy analyzer by a robotized vacuum chamber. Hence after an etching process, XPS spectra were recorded as function of take-off angle and the integrated intensities of the core-level peaks were used to obtain chlorine concentration and chemical state information from different depths of the sample, thereby permitting non-destructive characterization of chlorine profile in thin silicon oxide films. Material etch rates were measured in real time by in situ multi-wavelength ellipsometry.

When the plasma is pulsed, two parameters can be adjusted, namely the frequency of the pulse and the duty cycle. While the frequency has only a small influence on the etch rates in the investigated frequency range, our results demonstrate that a low duty cycle clearly modifies etch rate and can considerably improve the etch selectivity between silicon and silicon oxide. When a thin silicon gate oxide layer is exposed to very low energy etching conditions, a first step of chlorine incorporation is observed before etching. Preferential accumulation near the SiO_2/Si interface is observed and chlorine is shown to bond to both silicon and oxygen in multiple distinct chemical states.

4:20pm **PS1-ThA8 Fully Atomistic Profile Evolution Simulation of Nanometer-scale Si Trench Etching by Energetic F, Cl, and Br Beams**, ***H. Tsuda***, *T. Nagaoka, K. Eriguchi, K. Ono,* Kyoto University, Japan, *H. Ohta*, University of California, Santa Barbara

An atomic-scale understanding of interactions between chemically reactive plasmas and surfaces is required to establish nanometer-scale processing technologies. Various numerical studies based on molecular dynamics (MD) simulation have been reported so far, but these were limited to simulations of the simple blanket etching to estimate microscopic etching properties [1,2]. Here, we first report a fully atomistic silicon feature profile simulation using classical MD simulations. The potential form can be found in our previous papers [2,3,4]. F, Cl, and Br beams with a translational energy of 100 eV were used as reactive species. The surface area of Si (100) substrates was about 163 × 22 $Å^2$, where 3840 silicon atoms were initially located in the structure of diamond lattice. M ask patterns were introduced in the direction parallel to the short axis with periodic condition, in order to reproduce the trench etching feature. Then, the area without mask was 50 × 22 $Å^2$. By using our new atomistic profile evolution simulation, we investigated halogen plasma-surface interactions at sidewalls and bottom surfaces of nanometer-scale Si trench in detail. It was found that specific feature profiles with different gaseous species appear not only at the sub-micrometer-scale but also at the nanometer-scale etching, and the difference of surface reaction layer formation strongly affects the feature profile evolution during etching. For instance, fluorine beam etching showed that fluoride layer is formed on the entire surfaces containing sidewalls and bottom surfaces, thus giving isotropic etching. Chloride layer was thicker than fluoride and bromide layers, to give feature profiles of sidewall tapering. Bromide layer on bottom surfaces was thinnest among the three, and so the etching rate was lowest. So, it was cleared that the surface reaction layer formation strongly affects the feature profile evolution during etching. Our approach is essential as a reference for macroscopic or empirical profile simulation, where simulation sizes have been reduced recently. We also show some comparison between MD-based profile simulation and our empirical profile simulation (atomic-scale cellular model [5]).

[1] H. Ohta *et al*., J. Vac. Sci. Technol. A **19**, 2373 (2001).

[2] T. Nagaoka *et al*., J. Appl. Phys. **105**, 023302 (2009).

[3] H. Ohta and S. Hamaguchi, J. Chem. Phys. **115**, 6679 (2001).

[4] H. Ohta *et al*., J. Appl. Phys. **48**, 020225 (2009).

[5] Y. Osano and K. Ono, J. Vac. Sci. Technol. B **26**, 1425 (2008).

4:40pm **PS1-ThA9 Molecular Dynamics Simulations of Oxygen-Containing Polymer Sputtering and the Ohnishi Parameter**, ***G.K. Choudhary***, *J.J. Végh, D.B. Graves*, University of California, Berkeley

The effects of ion bombardment on polymer surfaces can be profound, with implications for all plasma-based pattern transfer processes that involve the use of polymer etch masks in lithography and etching. It is known that Ar^+ bombardment of various polymers results in the formation of a 1-2 nm deep cross-linked region at the exposed surface, and that virgin polymer sputtering yields can be several orders of magnitude higher than steady state yields after ion bombardment. [1]

In this talk, we report results from molecular dynamics (MD) simulations of Ar+ (~ 40 - 150 eV) sputtering of oxygen-containing polymers. The MD data are compared to available experimental results, with special focus on the so-called Ohnishi parameter, which has been shown to correlate with sputtering yields for many O-containing polymers. [2] The MD simulations match the published correlations well, and we present a quantitative model of sputtering for these polymers that shows why the Ohnishi parameter (a function of the polymer composition) is proportional to the steady state sputtering yield.

However, we also show that the Ohnishi parameter does not correlate with yields for other polymers, including polyfluoroethylene and polyethylene. The MD simulations show that the validity of this parameterization is dependent on whether or not the sputtering of the polymer transitions between ion-induced scissioning to cross-linking at steady-state.

Finally, we discuss the implications of the dynamics of ion-induced surface cross-linking for synergistic photoresist roughening that occurs in plasmas, especially in the presence of vacuum ultraviolet photon and/or beaming electron exposure.

[1] J. J. *Végh, D. Nest, D. B. Graves et al. " Near-surface modification of polystyrene by Ar+: molecular dynamics simulations and experimental validation" Applied Physics Letter, vol. 91, pp. 233113-1-3, 2007.*

[2] H. Gokan, S. Esho, and Y. Ohnishi, "Dry etch resistance of organic materials," J. EZectrochem. SOC., vol. 130, pp. 143-146, 1983.

5:00pm **PS1-ThA10 Charge Trapping and Valence-band Structure of VUV-Irradiated BEOL Dielectrics**, ***J.L. Lauer***, *J.L. Shohet,* University of Wisconsin-Madison, *Y. Nishi,* Stanford University, *A. Antonelli*, Novellus Corporatiion

The minimum spacing between conductive lines in advanced integrated circuits (ICs) continues to decrease with each generation of technology. As a result, the long-term reliability of ICs is becoming increasingly dependent on the reliability of the intermetal dielectrics which often become damaged during back-end-of-the-line (BEOL) processing. Dielectrics used in BEOL structures are often irradiated with photons of various energies during plasma processing, charge annealing, and curing of porous materials. In particular, processing plasmas produce significant amounts of vacuum ultraviolet (VUV) radiation which are, among other processes, capable of creating electron-hole pairs within dielectrics. As a result, VUV radiation has an impact on the electrical conductivity of dielectrics during plasma processing which can either contribute to or mitigate trapped charge within dielectrics. We compare the charging response of 50, 250, and 450 nm of SiOCH, SiN, SiCO, SiCN, and SiC dielectrics on Si substrates after irradiation to vacuum ultraviolet (VUV) radiation. We choose to irradiate the dielectric layers to a photon energy of 9.5 eV because photons with this energy are often emitted from processing plasmas that contain oxygen, i.e. ashing and etching plasmas. The charging response of the dielectrics was evaluated by measuring the surface potential on the dielectrics with a Kelvin probe after irradiation with several doses of 9.5 eV photons. The surface potential on all of the dielectrics after VUV irradiation was positive due to the accumulation of positive charge by traps located within the dielectrics. By comparing the surface potential on several thicknesses of dielectrics after VUV irradiation we can estimate the location within the dielectric the charge is trapped. The surface potential on SiOCH layers of varying k-values after VUV irradiation indicates the presence of both negative- and positive-charged traps. From VUV-spectroscopy, we determined the SiOCH layers have electron traps located 0.8 eV below the conduction-band edge and hole traps located 1.4 eV above the valence-band edge.

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Plasma Science and Technology
Room: B2 - Session PS2-ThA

Plasma Diagnostics, Sensors, and Control II
Moderator: C.A. Wolden, Colorado School of Mines

2:00pm **PS2-ThA1 Absorption Spectroscopy Diagnostics of a Dual-Frequency Capacitive Dielectric Etch Tool using Ultraviolet Light-Emitting Diodes**, ***J.-P. Booth***, CNRS/Ecole Polytechnique, France, *J. Bredin*, LPP, France, *G.A. Curley*, LPN/CNRS, France

Dual–frequency capacitively-coupled etch reactors using Ar/fluorocarbon/O_2 mixtures are widely employed for etching of dielectric films for integrated circuit manufacture. CF_x free radicals play an important role in the gas-phase and surface chemistry controlling etching and polymer deposition. The CF_2 radical is the most abundant, and its density can be measured by UV absorption via the A-X band (230-270 nm). Previously Xe arc lamps have been used for the absorption light source, but these sources are rather unstable, limiting the sensitivity of the technique, as well as being cumbersome and relatively expensive. We have successfully replaced the Xe arc with UV light-emitting diodes. The baseline stability is of the order $2x10^{-4}$, compared to $1x10^{-3}$ with an arc lamp. We determined the variation of the CF_2 density as a function of gas composition and power in a modified 2 + 27MHz commercial etch reactor operating in $Ar/C_4F_8/O_2$. As expected, the CF_2 density decreases rapidly as the O2/C4F8 ratio is increased. The CF_2 density increases with RF power at both frequencies, but is most affected by 27 MHz power. There is speculation that CF_2 may play an important role in either or both the creation and destruction of F- negative ions. However, we did not find any simple correlation between CF_2 density and electronegativity (as determined from electron density and ion flux measurements).

We also attempted to measure the F^- negative ion density by the continuum absorption below 365 nm. However in this case we observed a broad but structured absorption when the O2/C4F8 ratio is small. This absorption is too intense to be attributed to F^-, and we speculate that it is due to unsaturated CxFy oligomerisation products.

We wish to thank the Lam Foundation for financial support.

2:20pm **PS2-ThA2 On-wafer Monitoring for UV/VUV Photon Irradiation during Plasma Processes**, ***B. Jinnai***, *S. Fukuda, H. Ohtake,* Tohoku University, Japan, *E.A. Hudson,* Lam Research Corp., *S. Samukawa*, Tohoku University, Japan

Plasma processes are indispensable for the fabrication of ULSI devices. In plasma, there are many activated species, such as charged particles, radicals, and photons. By using these species, etching and film deposition can be achieved. UV/VUV photon irradiation from plasma can cause serious problems because UV/VUV photons can be absorbed in films and generate defects, which may cause degradations of device characteristics. In order to overcome this issue, it is important to understand characteristics of UV/VUV photon irradiation from plasma, such as UV/VUV spectrum and its absolute intensity (photon flux). To investigate these characteristics of UV/VUV photon irradiation from plasma, a VUV spectrograph can be used. A VUV spectrograph is, however, generally expensive and large system, so it is difficult to install. Also, spectra data obtained from a spectrograph is not always corresponding to the information of UV/VUV photon irradiation incident to wafers, due to the different field of view. In this study, we measured plasma properties on a commercial capacitively-coupled dielectric etch reactor using a VUV spectrograph and our developed on-wafer monitoring technique. The on-wafer measurement is based upon plasma-induced current in SiO2 and SiNx thin films. Furthermore, we develop the neural network (NN) modeling method based on the data from our developed on-wafer monitoring technique. By using this method, we could successfully predict the profiles of the UV/VUV spectrum. From the current measured by the on-wafer monitoring technique, we calculated the absolute intensity of UV/VUV photons. The on-wafer monitoring technique has many advantages for the investigation of UV/VUV photon irradiation during plasma processes, and can be applied to the prediction of device damages induced by UV/VUV photon irradiation from plasma.

2:40pm **PS2-ThA3 Influence of Argon Metastables on the Rotational Temperature of Nitrogen in Inductively Coupled Ar/N_2 Plasmas**, ***J.-S. Poirier***, *J. Margot, L. Stafford, P.-M. Berube,* Universite de Montreal, Canada, *M. Chaker*, INRS-EMT, Canada

In low-pressure discharges commonly used for materials processing, neutral gas temperature are routinely determined from the rovibronic structure of N_2 inserted as a tracer. This is realized by comparing the measured emission intensities of the bandhead and the violet-degraded tail of the second positive system of N_2 ($C^3\Pi_u$ v' -> $B^3\Pi_g$ v'') to the prediction of a model with the rotational temperature, T_{rot}, as the adjustable parameter. Such measurements are usually performed using the most intense (v',v'')=(0,0) and (0,2) bands at 337.1 and 380.5 nm. However, in argon-containing plasmas, these bands typically yield temperatures larger than those obtained from other methods such as Doppler-shifted laser-induced fluorescence (D-LIF). Hypotheses for such discrepancy vary; either the emitting $C^3\Pi_u$n'=0 level (11.026 eV above the ground state) could be populated by the $^3P_0$ and $^3P_2$ argon metastables (11.723 and 11.548 eV above the ground state) or the spatial non-uniformity of the plasma could skew D-LIF measurements. In this work, we examined the influence of Ar metastables on the rotational temperature of N_2. We compared T_{rot} values obtained from different N_2 bands, notably (0,0), (0,2), (1,0), and (4,2) to a less conventional plasma sampling mass spectrometry (PSMS) technique in which the Ar plasma on-to-plasma off signal intensity ratio is linked to the gas temperature. These measurements were performed in an inductively coupled 98%Ar/2%N_2 plasma as a function of pressure and absorbed power. We show that N_2 bands with v'≤2 generated much higher T_{rot} values than the (4,2) band or the PSMS. For example, for a 20 mTorr, 1000 W Ar plasma, the (0,0), (0,2), (1,0), (4,2), and PSMS yielded temperatures of 973, 715, 920, 485, and 415 K, respectively. We then computed the reaction rates for excitation of the $C^3\Pi_u$ v'=0 level by collisions with Ar metastables, R-Ar^m, and by electron-impact, R-e, from the ground state. The densities required as inputs for those calculations were measured by Langmuir probe for electrons and, for the metastables, were determined from a global model. We found that that the ratio of the temperatures obtained from the (0,0) and (1,0) bands to that of the (4,2) band increased quasi-linearly with the R-Ar^m-R-e ratio, going from 1.5 to 2 as the Ar metastable-to-electronic excitation rate ratio increased from 0.01 to 0.1. Since Ar metastables can have a strong influence on rotational temperatures even for R-Ar^m-R-e ratio as low as 0.01, accurate gas temperature measurements in mostly Ar plasmas thus require analysis of bands for which v'≥3 as these levels (e.g. 11.74 eV for $C^3\Pi_u$ v'=4) are above the $^3P_0$ Ar metastable level.

3:00pm **PS2-ThA4 Electron Temperatures and Electron Energy Distribution Functions in Dual Frequency Capacitively-Coupled CF_4/O_2 Plasmas, Measured with Trace Rare Gases-Optical Emission Spectroscopy (TRG-OES)**, ***Z.Y. Chen***, *V.M. Donnelly, D.J. Economou,* University of Houston, *L. Chen, M. Funk, R. Sundararajan*, Tokyo Electron America

Dual-frequency capacitively coupled plasmas (2f-CCP) used in the fabrication of modern integrated circuits may provide quasi-independent control of ion flux and energy. The accurate determinations of the electron temperature (T_e) and the electron energy distribution function (EEDF) are important for understanding plasma behavior and optimizing plasma processes in 2f-CCPs. In this study, measurements of T_es and EEDFs in CF_4/O_2 plasmas generated in a 2f-CCP etcher were performed as a function of pressure, applied RF power, and O_2 feed gas content by using trace rare gases-optical emission spectroscopy (TRG-OES). The parallel plate etcher was powered by a high frequency (60 MHz) "source" top electrode, and a low frequency (13.56 MHz) "substrate" bottom electrode. 80%CF_4+20%O_2 or 90%CF_4+10%O_2 plasmas were ignited at pressures ranging from 4 to 200 mTorr, top RF powers of 500 and 1000 W, four different bottom RF powers (0, 100, 300 and 500 W), and three different wafers (Si, Al and anodized Al). T_e was measured across the plasma at a height of 5 mm above the lower electrode. For Si substrates, T_e increased with increasing pressure between 4 and 20 mTorr (typically from 5 to 6.5 eV). The dependence of plasma electronegativity on pressure may be responsible for this behavior. T_e decreased rapidly with increasing pressure in the 20-60 mTorr range, and then slowly decreased with further increases in pressure to 200 mTorr, where T_e = 2.4 to 2.7 eV. Increasing the applied bottom RF power resulted in higher T_e, caused by enhanced stochastic heating of electrons with increasing low frequency voltage. Over the entire pressure range investigated, T_es in 90%CF_4+10%O_2 plasmas were similar to those in 80%CF_4+20%O_2 plasmas. The EEDFs exhibited bi-Maxwellian characteristics with an enhanced high energy tail, especially at pressures >20 mTorr. Different dependences of T_e on pressure and applied top and bottom RF powers were observed for Al and anodized Al wafers.

3:40pm **PS2-ThA6 Laser and LED based Optical Diagnostic Techniques Applied in Industrial Plasma Etch Reactors**, ***N. Sadeghi***, Université Joseph Fourier de Grenoble and CNRS-UJF-INPG, France, *G. Cunge, D. Vempaire, M. Touzeau, R. Ramos*, CNRS-UJF-INPG, France **INVITED**

External cavity tunable diode lasers (DL) and Light Emitting Diodes (LEDs) are cost effective and easy to use tools that can be easily implemented for the diagnostics of process plasmas. We have used these techniques to characterize plasmas produced in several industrial etch reactors (Applied Materials and LAM Research) and to better understand the interaction mechanisms of the plasma with surfaces present: wafers or/and reactor walls.

Using near infrared DLs, we deduce the gas temperature in different silicon etch plasmas (Cl_2, CF_4, SF_6,..) from the Doppler width of absorption lines from argon metastable atoms when traces of argon is added to the process gas [1]. Absorption and Laser Induced Fluorescence experiments with a blue DL permits to map up the angular dependent velocity distribution function of aluminum atoms sputtered from a RF biased Aluminum wafer under argon ion bombardment [2].

We have shown that the sensitivity of Broad Band Absorption Spectroscopy (BBAS) can be enhanced by at least one order of magnitude when a LED is used as a light source [3]. Thanks to the high stability of the LEDs, it is also possible to perform time-resolved measurements of radicals densities in pulsed plasmas [4]. With a 350 nm LED, the time variation of Cl_2 density down to 3 mTorr can be measured with a time resolution of about 10 millisecond [3]. With a 275 nm LED, we have measured the decay time in the afterglow of the BCl radical produced in BCl_3/Cl_2 plasmas. It has been shown that the main loss mechanism of BCl radical is its gas phase reaction with Cl_2 to form BCl_2 molecule [4].

[1] G. Cunge, R. Ramos, D. Vempaire, M. Touzeau, M. Nejbauer, and N. Sadeghi, JVST A **27**, 471 (**2009**)

[2] R. Ramos, G. Cunge, M. Touzeau, and N. Sadeghi, J. Phys. D: Appl. Phys. **41,** 152003 (**2008**)

[3] G.Cunge, D.Vempaire, M.Touzeau and N.Sadeghi, Appl. Phys. Letters **91**, 231503 (**2007**)

[4] D.Vempaire and G.Cunge, Appl. Phys. Letters **94,** 21504 (**2009**)

4:20pm **PS2-ThA8 Monitoring of Atomic H and Cl Surface Loss Kinetics by Time-Resolved Optical Emission Spectroscopy in an ICP Reactor used for Etching III-V Materials**, ***G.A. Curley***, *L. Gatilova, S. Guilet, S. Bouchoule*, LPN-CNRS Upr20, France

A study is undertaken of the loss mechanisms of H and Cl atoms in an inductively coupled plasma used for the etching of III-V materials for photonic device fabrication. A better understanding of these mechanisms may allow us to refine our previous kinetic models of Cl2/H2-based plasma used to anisotropically etch InP-based devices [1], and be useful for monitoring the reactor walls state. The study is also of interest for Cl2/HBr-based plasma chemistries.

The plasma phase is diagnosed using a time-resolved optical emission spectroscopy technique often referred to as pulsed induced fluorescence (PIF). In previous PIF studies, the plasma is pulsed with a standard TTL signal and a short probing pulse (0.05 to 1 ms) is added to scan the afterglow. In our case we extract the fluorescence signal directly from the rising edge of the plasma ignition and therefore only standard pulse operation of the RF generator is required.

In principle the evolution of various radical densities in the afterglow could be followed with the PIF technique by varying the duration of the interval between two successive pulses (the off time). In this study we monitor the evolution of hydrogen and chlorine radicals to deduce their surface recombination coefficients. The plasma is pulsed with an off-time ranging from 200 µs to 100 ms. The on-time is chosen for steady state conditions to be reached. The targeted pressure value lies in the range of 0.5 mTorr to 10 mTorr.

In the case of hydrogen, comparing the increase rate of H2 to the decay rate of H allows us to estimate if surface recombination mechanisms other than H(g) + H(s) -> H2 have to be considered. We therefore monitored both the H-alpha (656.3 nm) the Fulcher-alpha (602nm) line of H2. By pulsing the plasma with long off-times we can verify that emission from dissociative excitation of H2 is negligible under our experimental conditions.

The typical recombination coefficient of H in our reactor, with SiOAlCl passivated walls, has been found to be around 0.01. More interestingly the growth rate of H2 is at least two times higher than the decay rate of H. We will therefore discuss two possibilities that may explain this experimental observation:

1) the existence of a competing loss mechanism for H2;

2) the existence of another loss mechanism for H-atoms. This possibility was proposed in a study of the side-wall passivation of InP etched with Cl2/H2 chemistry [1], where H(g) + Cl(s) -> HCl was assumed to favor the removal of Cl from the passivation layer.

Finally, the PIF technique is evaluated for the first time in chlorine plasmas to deduce the surface loss coefficient of chlorine atoms.

[1] L. Gatilova et al, JVST A 27 (2009) 262

4:40pm **PS2-ThA9 Real Time Control of an Inductively Coupled Plasma Simulation**, ***B.J. Keville***, *M.M. Turner*, Dublin City University, Ireland

Process yield in many plasma assisted processes may be improved significantly by real time, closed loop control of certain plasma species. This paper describes the closed loop control of a low pressure, inductively coupled plasma simulation. The plasma simulation consists of a global model of the plasma chemistry coupled to an equivalent circuit. The equivalent circuit incorporates an impedance matching box and an model of power coupling from the antenna into the plasma which has been derived from the wave equation and the two term solution to the Boltzmann equation. In addition, mass flow controller models and gas flow transport delays are included in the simulation. The design of effective, real time, closed loop control algorithms is facilitated by simple, control-oriented, dynamical models of the relationship between actuators (inputs) and the process quantities to be controlled. The paper will indicate how the parameters of a control algorithm may be determined from the process model (model-based control) in order to guarantee a robustly stable closed loop response. In general, process measurements are noisy and may not provide direct estimates of process quantities to be controlled. For example, estimates of atomic oxygen density obtained from optical emission spectroscopy are ambiguous due to dissociative excitation. Furthermore, many process parameters such as wall sticking coefficients are extremely difficult to estimate and may change due to chamber seasoning. The paper will indicate how an optimal state estimator may be used to improve estimates obtained from optical emission spectroscopy and how such estimates may be used to adapt the control algorithm in real time in order to guarantee process stability despite changes in process parameters.

5:00pm **PS2-ThA10 Wafer Temperature Response During Plasma Etching and Applications to Chamber Matching**, ***J. Shields***, *C. Gabriel*, Spansion, Inc.

As dimensions shrink, wafer temperature plays an increasingly important role in plasma etch process control. Temperature, however, is usually only monitored indirectly by measuring the chuck temperature or the coolant temperature during processing. To address these issues, we have employed the wireless KLA SensArray Integral wafer to measure the actual wafer temperature at 65 locations during wafer processing in a dielectric etch chamber with three different RF frequencies available. The Integral wafer records the temperature up to several times per second on internal memory, which is then downloaded to a computer after processing is completed. We conducted tests with no RF power, to determine effect of upper electrode and lower electrode temperatures on the wafer. We then measured the temperature response under variable RF excitation conditions for three different process chemistries utilized for dielectric and organic etching. For each process chemistry, comparisions between different excitation frequencies and combinations of frequencies were performed. The dependence of wafer temperature average and uniformity on backside helium cooling was determined, including a series of tests with no backside helium to isolate the effect of just RF delivered power. Finally, the promising application of this technique to chamber matching activities was analyzed.

5:20pm **PS2-ThA11 Plasma Etch Chamber Wall Deposits – Impact on Etch Species Density and Evaluation of Cleaning Procedures**, ***D. Dictus***, *D. Shamiryan, V. Paraschiv, S. Degendt, W. Boullart, M.R. Baklanov*, IMEC, Belgium, *C. Vinckier*, KU Leuven, Belgium

During the last ten years there has been a growing awareness about the impact of the plasma etch chamber wall condition on the density of reactive species in the etch chamber. This is especially the case for ICP chambers at low pressure (5-80mTorr) where gas phase diffusion and recombination at the reactor wall can be a dominant loss mechanism for reactive species. The majority of the studies are carried out for reaction chambers, coated with SiOCl or CF_x -based polymers.

In this paper we expanded the study to metal deposits such as titanium and tantalum which are frequently used for metal gate application in front-end-of-line, or as hard mask material for low-k etching in back-end-of-line. Additionally we made an evaluation of the cleaning procedures to remove these metals from the reactor walls.

CF_x-based polymers where deposited by igniting a polymerizing plasma, while Si, Ti and Ta were deposited by etching Si, TiN and TaN, respectively, in $Cl_2/HBr/O_2$ plasmas. The composition of the chamber wall

deposits was investigated by XPS analysis of so-called 'floating samples'. Relative density variation of reactive species (Cl, Br, O and F) in "contaminated" chambers was analyzed by actinometry. For the actinometry experiments we added 5% Ar to respectively Cl_2, HBr, O_2 and SF_6 plasmas and we related the peak intensities to the Ar 750nm peak. Our results indicate that the effect of the metal deposits is very similar to the CF_x-based deposits. We can summarize this as a lowering of all tested species densities when the chamber walls contain metal(oxide) traces. By comparing our data with previously published results we can also estimate a recombination probability.

Next to the study on density variations of reactive species we investigated how these metals are best cleaned from the chamber walls. This is again done with actinometry, by comparing the data of 'clean' and 'coated' chamber walls. For CF_x based coatings and SiOCl coated chambers the cleaning procedure is well known and is mostly done with O_2 and SF_6 based plasmas respectively. For the metals however we found that titanium should be cleaned with Cl_2 plasma and for Ta we observed that none of the tested chemistries was able to quickly remove it. Since our XPS data indicate that the Ti and Ta on the walls is partially in the form of TiO_2 and Ta_2O_5 this is not a surprising result. Finally, we did observed that it's possible to clean both metals with BCl_3 or $SiCl_x$ containing plasmas but this is beyond the scope of this work.

Plasma Science and Technology
Room: Hall 3 - Session PS-ThP

Plasma Science Poster Session

PS-ThP1 3D Numerical Modeling and Experimental Characterization of Internal Antenna Type Inductively Coupled Plasma System for Nitriding of Bipolar Plates for PEMFC(Polymer Electrolyte Membrane Fuel Cell), ***J. Joo***, *W. Yang,* Kunsan National University, Republic of Korea*, J. Lee*, Seoul National University, Republic of Korea

Bipolar plates for PEMFC(polymer electrolyte membrane fuel cell) are crucial in determining service life of hydrogen fuel cells. The required anti-corrosion characteristics is very hard to meet with commercial materials, e.g. 316 stainless steels while keeping other requirements, e.g. electrical conductivity, mechanical formability and cost. Thin film coatings could be substitute solution but fairly marginal due to its relatively high cost. Second option is surface nitriding using high density plasma sources with appropriate substrate bias. Plasma nitriding at high temperature upto 800°C is a stable technology for automobile parts and tools. Stainless steels do not allow to go over 500°C due to its microstructural phase transformation. Low temperature, high rate nitriding technology is very crucial technique in this field. Bipolar plate is in a thin sheet form of 300 x 300 mm as thin as 0.5 mm. We used internal antenna type inductively coupled plasma as a source of nitriding species. The mixing ratio of nitrogen and hydrogen was varied to give optimal plasma generation condition. Plasma diagnostic techniques, e.g. Langmuir probe measurement, optical emission spectroscopy, and biasing voltage/current waveform measurements were used to characterize the process. For optimal design of industry scale systems, we used a 3D computational fluid dynamic code (CFD-ACE+). Number of antenna turns, relative positions of antenna and loaded sheets, gas pressure and composition were varied and diagnosed experimentally. In addition, substrate biasing schemes were studied. Final anti-corrosion characteristics showed that pulsed dc bias of 50 kHz with 600 W of ICP was giving best corrosion current density among others; 316 stainless steel, Cr, CrN with dc bias.

PS-ThP2 Multidimensional Plasma Simulations of an SF_6/O_2 Etch, *J. Tennyson,* ***S. Harrison***, University College London, UK*, J.J. Munro, D. Brown*, Quantemol, UK

Sulfur Hexafluoride (SF_6) is the plasma processing gas that is used industry-wide in a range of processes for the dry etching of silicon. However, the performance and efficiency of different processes and machines can vary widely. Through simulation we can gain significant insight into the optimization problem and provide a low cost means for further development.

SF_6 is also very bad for the environment with a Greenhouse Warming Potential that is 22,000 times that of CO_2. Therefore it is vital that SF_6 is used sparingly and efficiently in every process. Here, simulation can help to find ways of remediating harmful waste gases and optimize the process for typical processing goals (e.g. etch rate, uniformity) as well as improving SF_6 consumption efficiency and other environmental measures.

Here we present an full chamber 2D simulation of an SF_6/O_2 silicon etch process, building upon previous calculations of SF_6 plasma chemistries using Quantemol-P [1]. Etch rate, pressure and power trends along with chamber wide contour plots of gas-phase species concentrations and fundamental plasma properties are considered.

To perform these calculations and build this model a new software tool is being constructed and will be demonstrated. The plasma simulation itself is run using a set of algorithms and codes based on HPEM [2]. The new code will integrate with outputs from Quantemol-N [3], which provides data on molecular processes, and Quantemol-P. It will provide

a set of design and specification tools, along with an expert system for running HPEM and a design of experiments (DOE) type calculation system.

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PS-ThP3 Semi-analytical Model of Standing Wave and Skin Effect in Large-area RF Discharges, ***M. Klick***, Plasmetrex, Germany

Large area plasma coating becomes more important with increasing diameter of semiconductor wafers and thin film Si solar cells. The layer characteristics depend on the plasma, the uniformity depends mainly on the plasma sheath voltage at the substrate via the ion energy distribution and the corresponding back-etch rate. Therefore the modeling of large-area CCPs is increasingly important. In particular the skin and standing wave effects must be involved, beside the non-homogeneous distribution of chemically active species in plasma these effects are the major root causes of non-uniform interaction plasma and surrounding solid bodies.

A semi-analytic, cylindrical and 2d plasma model based on the full set of the Maxwellian equations was developed. It involves also the non-uniformity and nonlinearity of the plasma sheath as nonlinear boundary condition. It involves dynamic electron effects by a fluid model for the plasma bulk and nonlinear mechanisms by a nonlinear sheath model.

The model includes nonlinear effects and provides so the dependence of the Fourier spectrum of the local RF current on geometry, plasma density, and the electron collision rate. The ratio of the excitation frequency to the resonance frequencies of the spatial mode is found to determine the nonuniformity caused by the standing wave. The collisional skin depth can be also estimated. Thus the mean sheath voltage varying along the grounded electrode through both standing wave and skin effect can be easily calculated and understood by means of a semi-analytical model.

Both a center and edge maxima or even spatial oscillations in the mean sheath voltage at the grounded electrode can be observed. This is in agreement to experimental results of Si deposition used for comparison. It can be also shown that well-known terms as symmetry loose sense for very 'flat' RF discharge systems, they can be symmetric in the center and asymmetric near the edge.

PS-ThP4 U-shaped Internal Inductively Coupled Plasma Source with a Ferrite Module for Roll-to-Roll Processing, ***S.P. Hong***, *J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Flexible display devices are being investigated by many researchers as a potential next-generation display. Roll-to-roll plasma processing is one of the important techniques for flexible display processing. For the fabrication of flexible display devices by the roll-to-roll plasma processing, not only highly uniform plasma processing but also high processing rates are required to increase the throughput of the processing. In particular, for the use of low-temperature substrates such as plastic substrates, the processing at the temperature lower than 100 ℃ is required.

In this work, we present a line-type, high-density plasma source composed of a U-shaped internal antenna for an inductively coupled plasma (ICP) operated at 2 MHz and with a ferrite module installed on the antenna of the ICP source. The 2300 mm long χ 740mm wide ICP source showed the plasma density of about $3.1\ \chi\ 10^{11} cm^{-3}$ at 3.5kW with the plasma uniformity less than 11% along the antenna line. The plasma characteristics of the source were measured using a Langmuir probe (Hiden Analytical Inc., ESP), and the electrical properties of the line-type, internal antenna were measured using an impedance analyzer (MKS Inc.).

PS-ThP5 Self-Consistent Electrodynamics of Very High Frequency Plasma Discharge Chambers, ***Z. Chen***, *J.A. Kenney, S. Rauf, K. Collins*, Applied Materials, Inc.

Very high frequency (VHF) radio-frequency (RF) sources are used for many plasma processing applications including material etching and thin film deposition. However, when chamber dimensions become commensurate with RF wavelength, electromagnetic effects have a significant influence on plasma behavior. We present a 2/3-dimensional model for self-consistently studying both electrodynamic and plasma dynamic behavior of complete RF plasma discharge chambers. The model is fully self-consistent in the following senses: (1) Maxwell's equations and transport equations for charged and neutral species are coupled and solved explicitly in time domain; (2) The complete RF plasma discharge chamber including the RF power delivery sub-system, electrodes and plasma domain is modeled all together and simultaneously; and (3) The RF source is naturally applied onto the transmission line of the RF feed system in the form of an electromagnetic wave rather than hard imposition of assumed RF sources onto the electrodes or on the boundary of plasma. In the model, Maxwell's equations are discretized using the Finite-Difference Time-Domain (FDTD) method, and plasma discharge is modeled by solving the time-dependent continuity equations for charged and neutral species, drift-diffusion approximation for specie fluxes, and the electron energy conservation equation. Such a systematic approach is equally applicable to both capacitive and inductive discharges. It is useful for understanding not only electrodynamic effects in large-area VHF plasma chambers, but also the impact of asymmetric parts in RF systems and electrodes on the symmetry and uniformity of electric field and plasma in discharge region, which is of significant interest in industrial applications of RF plasma

chambers. We first apply the model to study the impact of azimuthally asymmetric dielectric and conducting perturbations in the RF feed system on plasma uniformity. Then we examine the effect of transmission line length and impedance on plasma profile, especially in regimes close to resonance. We also explore the potential application of VHF source in large area (> 5 m^2) capacitively coupled plasmas. Based on the model, we have been able to identify a variety of design approaches for ensuring electric field and plasma symmetry and uniformity in discharge region.

PS-ThP6 Characterization of a Power Splitter for Multi-Tile Plasma Source for VHF/UHF PECVD Film Growth, *A.R. Ellingboe,* Dublin City University, Ireland, ***T. Michna***, Phive Plasma Technologies, Ireland

A novel divide by arbitrary-N power divider for use in the 100-500 MHz frequency range will be introduced. Electrical characterization of the power divider will be reported. The system has been successfully applied to an extensible, multi-tile plasma source operating from below 100 MHz to over 400 MHz. The plasma is found to light uniformly over the electrode surface for electronegative and electropositive gasses; and a 300mm diameter plasma has been sustained at under 15 Watts.

In multi-tile electrode solutions, the plasma load on the power splitter can result in spatial inhomogeneities in plasma creation; this fault is overcome by careful design of the system. A narrow-gap 300mm by 400 mm plasma is found to light uniformly over the electrode surface for electronegative and electropositive gasses at pressures from 10 mTorr to 3 Torr; plasma has been sustained across the full volume at under 25 Watts.

PS-ThP7 Experimental and Numerical Investigations of a Hollow Cathode Plasma Source for Microcrystalline Silicon Deposition, ***F.C. Tung,*** ITRI/MSL, Taiwan, R.O.C., *T.C. Wei,* Chung Yuan University, Taiwan, R.O.C., *S.W. Chau,* National Taiwan University of Science and Technology, R.O.C., *P.S. Wu,* ITRI/MSL, Taiwan, R.O.C, *C.-H. Lin*, Chung Yuan University, Taiwan, R.O.C.

Microcrystalline silicon thin films were grown by plasma enhanced chemical vapor deposition from a mixture of silane and hydrogen gases at low temperature. The effect of process parameters on the velocity, temperature and species concentration profiles are reviewed in this article. Several numerical simulation and in-situ plasma diagnostics on a hollow cathode plasma source and a process chamber are compared, which can be used to characterize the plasma properties. A global plasma model is developed for the plasma source and a CFD model is developed for the process chamber. Diagnostics of the plasma are carried out using a Langmuir probe and optical emission spectroscopy. Based on these investigations, an updated view on the role of the process parameters is presented.

PS-ThP8 Novel Long Linear-Type Microwave Plasma Source, ***C.C. Chang***, Industrial Technology Research Institute, Taiwan

A novel long linear-type microwave plasma source using a variably-reduced-height rectangular wave-guide as the plasma reactor has been developed. Microwave power is fed from the both sides of the wave-guide and is coupled into plasma through a long slot cut on the broad side of the wave-guide. The reduced height of the wave-guide is variable in order to control the coupling between microwave and plasma so that the plasma is able to attain better uniformity when extending the length of the linear-type plasma source.

PS-ThP9 Time Resolved Energy Distributions for Positive Ions in an Inductively-Coupled Plasma Reactor, ***J.A. Rees***, *C.L. Greenwood, D.L. Seymour*, Hiden Analytical, UK

The energy distributions of positive ions created in an inductively–coupled plasma have been examined using a Hiden EQP mass/energy analyzer. Time-averaged distributions were measured with and without the presence of a Faraday shield between the external RF excitation coil and the glass wall of the reactor. With the shield in position, the coupling of power into the plasma was purely inductive, but without it there was a significant capacitive contribution. The time-average distributions were measured both for continuous power applied to the plasma and for the case where the RF supply was pulsed. For this latter series of experiments, time-resolved distributions were also measured, and the decay in the energies of the ions as a function of time in the afterglow of the plasma was examined. The time-resolved data were obtained by gating the operation of the EQP analyzer either at the ion-counting detector of the instrument or, alternatively, by pulsing a grid mounted behind the sampling orifice of the instrument. The measured energy distributions were independent of the gating method. The distributions for the inductively-coupled and inductive/capacitive coupling are compared.

PS-ThP10 Influence of Sheath on Measurement of Electron Density in Frequency Shift Probe and its Application to Measurement of Electron Temperature, ***K. Nakamura***, *Q. Zhang, H. Sugai*, Chubu University, Japan

In advanced materials processing for manufacturing LSI devices, improvement of accuracy and repeatability has been required to achieve high performance plasma processes. In general, temporal variation of plasma components is believed to be one of reasons for the problems, so it is important to develop technologies for accurate plasma control. We have developed a frequency shift probe as a novel in-situ plasma monitoring technology. The probe enables us to measure an electron density from variation of resonance frequency of the probe head, and the density measurement is possible under minimum disturbance to the processing plasma because of its plane structure. Furthermore, the probe is applicable to a reactive plasma such as fluorocarbon plasmas since the deposited polymer has no significant effects on the resonance frequency. When the resonance frequency of the probe varies from f_0 (GHz) to f_r (GHz) by producing the plasma with the electron density of n_e, (10^{10} cm^{-3}), the value of n_e is given by $n_e=(f_r^2-f_0^2)/0.81$. However influences of a sheath formed around the probe have not been considered in the formula. In this work, sheath effects on the frequency shift probe were investigated based on finite difference time domain (FDTD) simulation, and it was examined how much influences on the measured density the sheath has. Furthermore, the frequency shift probe was tried to be applied to measurements of electron temperature using the sheath effects. As the sheath thickness increased, the resonance frequency decreased since effective permittivity of the media around the probe head decreased. Such a decrease of the resonance frequency was observed regardless of the slit width, however its dependence on the sheath width was affected by the slit width, and it became significant as the slit width decreased. The sheath width is proportional to Debye length, so the resonance frequency of the frequency shift probe is a function of electron density n_e and electron temperature T_e. This means that resonance frequencies obtained in two frequency shift probes having different sheath dependence gives an unique solution of n_e and T_e. Actually, in a experiment using a plasma produced with 13.56 MHz RF power up to 400 W at an argon pressure of 3 mTorr, the present method derived 7.5×10^{10} cm^{-3} in n_e and 4.8 eV in T_e which comparatively showed good agreements with values measured by a Langmuir probe.

PS-ThP11 High Performance of Compact Combinatorial Etching Process for Next Generation Plama Nano-Process, ***Ch.S. Moon***, *K. Takeda,* Nagoya University, Japan, *Y. Setsuhara,* Osaka University, Japan, *M. Shiratani,* Kyushu University, Japan, *M. Sekine, M. Hori*, Nagoya University, Japan

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, nano-leveled precise control has been indispensable to achieve the process requirements. However, up to now, it was an obvious fact that a lot of trials-and-error processes have been carried out in the development of plasma etching processes in which were characterized by external parameters (input power, working pressure, mixture gas ratio), since there has never been any scientific principle based on plasma science. We hereby propose the development of process map, Plasma Nano Science in which the process results are characterized by internal parameters (fluxes and energy distributions of ions, radicals, substrate temperature). For the breakthrough of next generation plasma nano-process guided by Plasma Nano Science, we have developed the combinatorial plasma etching process, in which a variety of results could be acquired by one trial. In this work, the compact combinatorial plasma apparatus was realized in inductively coupled H_2/N_2 plasma driven by two low-inductance (LIA) antennas for etching of organic low-k dielectric films. The spatial distributions of H and N radical densities were measured by vacuum ultraviolet absorption spectroscopy (VUVAS) system and RF-compensated Langmuir Probe (Scientific Systems Smart Probe^{TM}) was used to record the spatial distributions of electron densities, temperatures and energy distributions. In this paper, we present high performances of combinatorial etching process. Etching characteristics such as etch rate and profiles were analyzed in terms of internal parameters rather than conventional external parameters by controlling respective LIA antennas independently.

PS-ThP12 Tailoring of Substrate RF Bias Voltage Waveform for Arbitrary Energy Distributions of Bombarding Ions in Plasma Processing: Ion Energy Measurements, ***X.V. Qin***, *Y.-H. Ting, A.E. Wendt*, University of Wisconsin-Madison

In plasma etching of semiconductors for integrated circuit fabrication, positive ions are accelerated by a sheath electric field directed towards the substrate, where, upon impact at normal incidence, they enhance etching to produce anisotropic feature profiles. Varying the amplitude of a sinusoidal bias voltage waveform applied to the substrate electrode may be used to coarsely control the average energy of bombarding ions through its affect on the dc component of the sheath voltage, but the sinusoidal waveform

also produces a broad spectrum of ion energies under typical process conditions. A bias voltage waveform with its shape tailored for the purpose of producing ion energy distributions (IED) with one or two groups of ions with a narrow spread around selected energies has been previously utilized to highlight the significant role of the IED in fluorocarbon-based etching. Presented here are direct IED measurements made with an Impedans™ retarding field energy analyzer situated on the biased electrode. Measurements in a 10 mTorr helicon argon plasma in which ion flux and ion energy at the substrate are independently controlled clearly demonstrate the ability to predictably produce arbitrary IEDs at the substrate by tailoring the shape of the bias voltage waveform. Results to be presented for sinusoidal (500 kHz-10 MHz) and tailored (500 kHz) waveforms are compared to predictions based on computation of ion trajectories through the sheath electric field (assumed to instantaneously follow the Child-Langmuir Law), in order to evaluate the accuracy and limitations of this method. For the sinusoidal waveform, the expected broad, bimodal IED is produced, with a reduction in IED width with increasing frequency in agreement with model predictions. Under conditions where the sheath transit time of the ions is short compared to the RF bias period and where ion motion in the sheath is collisionless, tailoring of the waveform produces one or two peaks in the IED, and in the latter case, the energies and relative fluxes of the two peaks can be varied independently through waveform shaping.

*Support from the Lam Research Corporation and the UW NSF MRSEC are gratefully acknowledged.

PS-ThP13 Measurement of Electron Energy Probability Function in Dual-Frequency Capacitive Discharges, ***S.K. Ahn**, H.Y. Chang*, Korea Advanced Institute of Science and Technology

Changes in plasma characteristics depending on low-frequency power in dual-frequency capacitive discharges were found from the measurement of electrical characteristics and electron energy probability functions (EEPFs). It is shown that as the low-frequency (2 MHz) power increases for the fixed high-frequency (27.12 MHz) current, the ion bombardment energy and the ion flux onto the electrode increase simultaneously, and hence independent control of the ion energy and the ion flux is hardly achievable in dual-frequency capacitive discharges. It is also shown that the coupling between the low-frequency power and the ion flux originates from change in electron heating mechanisms when varying the low-frequency power. Depending on the discharge pressure, changes in the collisional electron heating in the bulk plasma and participation of the secondary electron emission in the ionization process are observed.

PS-ThP14 Time-resolved Fast Imaging of the Arcing in RF Discharge, ***Y.H. Kim**, H.S. Lee, H.Y. Chang*, KAIST, Korea

Arcing have become a fatal problem in TFT-LCD fabrication, semiconductor manufacturing, PECVD, and many other processes using plasma. Although modern plasma processing is using rf power, the arcing in rf plasma isn't well-known. We investigated the arcing in RF plasma. In order to generate the arcing, the dc-grounded rf (13.56 Mhz) power was delivered to argon plasma. The arcs are generated at high plasma potential (over 100 V), irregularly. We measured floating potential, discharge current and voltage during the arcing, and sparks were observed in arcing spots. Floating potential drastically decreased to almost ground potential, and both discharge current and voltage decreased to almost zero, too. As soon as floating potential decreased to ground, floating potential, discharge current and voltage return to steady state slowly more than decrease. These arcing signals show that the arcing perturb the rf plasma and that rf plasma transiently response. The discharge of sheath-capacitor by collective electron emission explain the transient behavior of plasma during the arcing. And, to confirm the collective electron emission, we imaged the arcing by using the ICCD (intensifed charge coupled device, ANDOR Technology Ltd.) camera with the maximum gate speed of 2ns. We checked the three regions in the aring. These are sheath breakdown region, arcing duration region and shaeth rebuilding region.

PS-ThP15 Design of a Kalman Filter for Plasma Process State Estimation and Control, *B.J. Keville, **M.M. Turner***, Dublin City University, Ireland

Real time, closed loop control of certain plasma species may potentially improve reproducibility and increase process yields. In order to investigate the feasibility of applying closed loop control to a plasma process, closed loop control of a plasma simulation was studied. This presentation concentrates solely on control issues, since the simulation was described in a companion presentation. The design of real time control algorithms is facilitated by simple, dynamical process models. The derivation of such a model from a much more complex simulation is presented, together with a stability analysis which indicates how the parameters of a real time control algorithm may be determined from such a model (model-based control). Process measurements may be indirect and, in addition, corrupted by process and measurement noise. Simple dynamical models may be used to construct model-based estimators such as the Kalman filter. The construction of such a filter to improve estimates obtained from optical emission spectroscopy is described in this presentation. Finally, the application of adaptive control to maintain closed loop stability despite changes in process parameters such as wall sticking coefficient due to chamber seasoning is presented.

PS-ThP16 Contamination Detection through OES in Conductor Dry Etch Process, ***C. Bevilacqua**, A. Marchelli, P. Petruzza, G. Fazio*, Numonyx

In a R&D fab, where different processes are performed on the same dry etching hardware, there is a strong need to monitor the status of the chamber, in terms of cross-contamination from the different etching species and their reactions products deposited on chamber walls, which can cause uncontrolled shifts in the processes.

Through this work we validate a new technology method for monitoring and reveal metal elements in dry etch conductor tool.

Changes in chamber wall conditions (e.g., chemical surface composition) are identified as one of the main causes of process drifts leading to changes in the process performance (etch rates, etch profiles, selectivity, uniformity, etc.). This effect is particularly critic when the same chamber is required to sequentially process metals and non-metal elements. Standard control procedures mainly based on XRF technology utilize wafer tests to perform the acquisition measurements with relevant down times and low frequency testing. It is known that different conditions of the chamber walls have great influence upon global system impedance (plasma + equipment hardware), which requires continuous tuning of the RF system in order to maximize the power transfer to the plasma.

The observation of optical emission (performed through a spectrometer directly installed on the tool) from a waferless He plasma allows to detect some variation of impedance due to different chamber conditions.

The choice of He as process gas for this test is mainly due to the fact that it is chemically inert; besides is allows minimum impact on consumable parts inside the equipment. By comparing the test described to standard quantitative technology, we are able to identify a cut off threshold - technology device-dependent - above which the decontamination procedure becomes mandatory.

The new test can be used at the end of each critical process like a waferless autoclean, in order to constantly monitor the status of the chamber and assure a safe and correct lot processing.

PS-ThP17 Spatial Evolution of the Electron Energy Distribution Function in a Microwave Surface-Wave Plasma, ***J.P. Zhao**, R.V. Bravenec, L. Chen, M. Funk, R. Sundararajan,* Tokyo Electron America, Inc., *C.Z. Tian, K. Ishibashi, T. Nozawa*, Tokyo Electron Technology Development Institute, Japan

Microwave surface-wave discharges operating within a wide power and pressure window can be used to produce large-area plasmas of densities exceeding $10^{11}/cm^3$. Due to its inherent diffusion characteristics, away from the discharge source one can expect a relatively high density, quiescent, uniform, and low-temperature single Maxwellian plasma near the wafer region. That is, one would have a unique plasma tool with totally decoupled source of discharge and wafer process region. These merits are highly desired in large-area microelectronic technologies, such as in plasma-enhanced chemical-vapor deposition and etching processes. Because of these promising features, we are trying to understand the mechanisms of the microwave surface-wave plasma such as electron heating and power absorption in the discharge region and the spatial evolution of plasma parameters in the entire plasma volume. Understanding the evolution of plasma parameters in the entire plasma volume would help the development of tools based on microwave surface-wave plasmas and the design of process recipes. The plasma source used in this work consists of a radial line slot antenna (RLSA) which transmits 2.45 GHz microwaves into a large quartz resonator disk which then couples to the plasma. The plasma parameters of a nitrogen plasma, e.g., electron energy distribution functions (EEDF's) are measured using a cylindrical Langmuir probe. EEDF measurements are carried out from 8 mm below the bottom surface of the resonator disk to the wafer surface, a span of ~140 mm in the vertical direction. A wide pressure-power range has been investigated, i.e., pressures from 20 to 800 mT and powers from 2 to 4 kW. Based on initial global-modal analysis of experimental observations, EEDF's are analyzed using a curve fitting method developed in-house that assumes electrons in the microwave surface-wave plasma consist of two Maxwellian distributions and a drifting Maxwellian that models a beam component.[1] The relative population and magnitude of these electron components vary as a function of vertical location in the plasma volume. High populations of energetic electrons with energies exceeding 20 eV are typically observed

near the resonator disk, i.e., the EEDF is dominated by the beam component. Away from the resonator disk, the EEDF transitions to two Maxwellians then thermalizes to a single cold Maxwellian of Te ~1 eV near the wafer surface. Pressure and power are found to have strong effects on the transition of the beam component to Maxwellian component. Particle-in-cell simulations[1] are conducted to understand the experimental observations.

[1]R. V. Bravenec et al., presentation at this conference.

PS-ThP18 Diagnostic Study of an rf-capacitively Coupled Plasma: The Breakdown of the Periphery Gap Regime, ***H.W. Chang***, *C.C. Hsu*, National Taiwan University, Taiwan

A diagnostic study of a radio-frequency capacitively coupled plasma of Ar, O_2, N_2, and He was performed to investigate the mechanism that dominates the breakdown of the periphery gap region. This plasma chamber has a cylindrical glass chamber with annular ring-shaped, powered electrodes with an adjustable height and a planar sample stage that serves as the grounding electrode. A voltage probe and a current probe were used to monitor the electrical characteristics of this plasma, and an optical emission spectrometer was used to monitor the optical emission spectra of the plasma. It is shown that as the (peak-to-peak) voltage at the powered electrode exceeds a critical value, the ignition in the region between the glass chamber wall and the grounding electrode occurs. Such a breakdown potentially leads to unstable and non-uniform discharge. A drop of the current and voltage were found to accompany the periphery region breakdown, and it was found that the pressure, gas type, and gap size are the decisive factors that dominate such a breakdown. The breakdown voltage increases with the decreases of the gap and with the decreases of pressure: in an Ar discharge under 80 mtorr, the breakdown voltage increases from 280 to 972 V as the sample stage-glass chamber wall gap decreases from 7 to 5 mm. Under 5 mm gap and 100 mtorr, the voltage at which the periphery region breakdown occurs for Ar, N_2, and O_2 are 577, 1470, and 2444 V while no breakdown occurs in He plasmas with the voltage up to 2560 V. While such a breakdown seems undesired in materials processing, we will show that a well-controlled transition could potentially be used to obtain a localized high-density region that could be useful for materials processing.

PS-ThP19 Real-Time Feedback Control of Radical Species by OES in a VHF Plasma for Microcrystalline Silicon Thin Film Deposition, ***C.H. Chang***, *C.C. Du, M.W. Liang, J.R. Huang,* Industrial Technology Research Institute, Taiwan, *Y.L. Chang, K.C. Leou*, National Tsing Hua University, Taiwan

Plasma deposition of intrinsic microcrystalline silicon (μc-Si:H) films with high deposition rates is a key process for the fabrication of high efficient thin-film solar cells. Recent studies have shown that the concentration of the radical species in hydrogen diluted silane plasma is time-dependent during the deposition process and results in inhomogeneous film growth that diminishes the solar cell efficiency. In this study, we developed a real-time feedback control system that corrects for the radical species variation in a VHF (40.68 MHz) PECVD reactor, via modulating the chamber pressure and silane dilution for depositing high quality μc-Si:H films. In this control system, trace rare gases-optical emission spectroscopy (TRG-OES) was used to determine the absolute species concentrations (e.q. Si, SiH_x, H) by deriving from their optical emissions. To convert the emission intensities into absolute number densities, a small amount of Ar was fed into the plasma to be as trace gas. Observed real-time variations in species signals were then compensated by using a proportional-integral (PI) feedback control algorithm. The system actuator was either or both of the pressure controller and the silane mass flow controller. The experimental results show that the OES intensities have obvious spikes after plasma is ignited and then decreases to a lower level at the first stage in about 10 seconds. This is because of the pressure unbalance between the throttle valve control and the expanded number density of gas induced by plasma heating and dissociation reaction in the chamber. After the transient of pressure unbalance, the intensity of H_α increases close to 20 % and the SiH^* decreases 10 % during the deposition in 10 minutes. This is believed to be due to the change of chamber wall surface condition. The deposited silicon films on the rf electrode, glass substrate and the other surface surrounds the plasma, grow continuously and affect the conditions for plasma. In the mean while, the closed-loop control can indeed stabilizes the radical species concentration within ± 1.5 % and has a good crystallinity control during the deposition process. Comparisons such as film growth structure and efficiency of solar cells deposited by closed-loop and open-loop controls will also be presented at the conference.

Plasma Science and Technology
Room: B2 - Session PS-FrM

Plasma Science for Medical and Biological Applications
Moderator: J. Hopwood, Tufts University

8:20am **PS-FrM1 Positive Streamers Propagating Inside Bubbles in Liquids**, ***N.Yu. Babaeva***, *M.J. Kushner*, University of Michigan

Pulsed discharges in liquids are often in the form of streamers. In most cases, streamers do not directly propagate through the liquid phase. Rather breakdown occurs inside bubbles and near gas–liquid interfaces. Often bubbles are purposely injected to facilitate breakdown. Such discharges have been extensively studied for their use in water treatment, surgery, decontamination and sterilization. Recent experiments have shown that streamers often preferentially propagate along the surface of a bubble immersed in a liquid instead of propagating along the axis of the bubble. In this talk, we discuss results from a computational investigation of the propagation of streamers inside bubbles immersed in liquids. We show that dielectric constant of a liquid determines patterns of streamer propagation. The model, *nonPDPSIM*, is a 2-dimensional simulator executed on an unstructured mesh in which Poisson's equation for the electric potential, and transport equations for charged and neutral species, and electron temperature, are solved. Radiation transport and photoionization are included by implementing a Green's function propagator. A bubble of humid air, $N_2/O_2/H_2O$ = 55/15/30 at atmospheric pressure is placed at the tip of a positive corona discharge immersed in a liquid of specified conductivity, σ, and permittivity, $\varepsilon/\varepsilon_0$. The bubble radii are 0.45 - 0.9 mm. We found that for low values of σ and $\varepsilon/\varepsilon_0$ the streamer propagates along the axis of the bubble. For large values of σ and $\varepsilon/\varepsilon_0$ the streamer propagates along the surface of the bubble. For essentially non-conducting liquids, the transition between axial and surface-hugging streamers occurs at $4 < \varepsilon/\varepsilon_0 < 8$, depending on the size of the bubble and voltage. Increasing conductivity lowers the value of $\varepsilon/\varepsilon_0$ at which the streamer becomes surface-hugging. These trends largely result from the refraction of the electric field by the curved interface of the bubble in the presence of a diverging electric field. The final pattern of the streamer path is additionally a function of bubble size and its position relative to the tip of the electrode, applied voltage and polarity.

8:40am **PS-FrM2 Atmospheric Plasma for the Degradation of Pollutants : The Promoting Effect of Water**, *S. Al Takriti, J.M. Giet,* Université Libre de Bruxelles, Belgium, *C. Pierard,* ArcelorMittal Research Liege, Belgium, ***F. Reniers***, Université Libre de Bruxelles, Belgium

Atmospheric plasmas have been used for a long time for the degradation of volatile organic compounds (VOC). In this study we focus on the degradation of non volatile organic compounds, like hexadecane and hexachloropropene, using an oxygen containing atmospheric plasma.

The kinetics of the reactions was followed by mass spectrometry, by tracking the m/z signal of the production of carbon dioxide.

The pollutants were degraded in a dielectric barrier discharge plasma chamber, operating at frequencies between 10 and 20 kHz, and at voltages between 1 and 4 kV. The plasma gas was either pure oxygen, or a helium/oxygen mixture. The promoting effect of water was studied by adding controlled amounts of water vapour to the gas mixture.

Optical emission spectrometry was used to characterize the plasma gas phase. More specifically, the oxygen emission lines, and the OH bands were followed, as a function of the plasma parameters.

It is shown that the degradation efficiency increases with the charge delivered in the plasma, as well as with the oxygen content.. A correlation is established between the oxygen OES emission line and the carbon dioxide production, for plasmas containing no water. For water containing plasmas, the oxygen line decreases, whereas the carbon dioxide production increases. The decrease of oxygen is interpreted in terms of consumption of the oxygen radical by water molecules to create hydroxyl groups, which are responsible for the increase of the degradation of the organic molecules. A simple global mechanism is proposed.

Acknowledgements : this work is funded by the IAP "physical chemistry of plasma-surface interactions - PSI" program from the Belgian Federal Government

9:00am **PS-FrM3 Challenges in the Numerical Simulation of the Plasma-Biomaterial Interaction**, ***Y. Sakiyama***, *D.B. Graves*, University of California, Berkeley **INVITED**

Nonthermal atmospheric pressure plasmas have received considerable attention in recent years. One emerging and promising application is the biomedical field. A wide variety of investigators have already demonstrated various biomedical effects of nonthermal plasmas, including sterilization/disinfection, blood coagulation, wound healing, tissue regeneration, etc. [1] The mechanisms of the plasma-biomaterial interaction are however only poorly understood. A central scientific challenge is therefore how to answer the question: "What plasma-generated species or plasma-created electric fields and currents, or any other effects of the plasma, are responsible for the observed biological effects?" Our modeling efforts are motivated by this question.

We have focused on the RF-excited plasma needle at atmospheric pressure and developed fluid models using the finite element method. Our simulation model successfully reproduced various experimental observations. For instance, our two dimensional model demonstrated that the plasma needle operates in two discharge modes: the corona-mode under low power condition and the glow-mode under high power condition. [2] The model showed that the plasma needle discharge strongly depends on the electrical properties of treated materials. [3] Also, we found that the ring-shaped emission pattern observed during bacteria treatment[4] was due to back-diffusion of air and Penning ionization and excitation of N_2 from He metastables. [5] Furthermore, results from a more complete model including humid air chemistry indicate that plasma-air interaction creates various neutral species via electron impact reactions near the treated materials. Those reactive neutrals (e.g. O, OH, NO) appear to have significant effects in the inactivation processes by the plasma needle.

In this talk, we will briefly review recent progress in biomedical applications of gas plasmas. Then, our modeling results are discussed in detail.

1 G. Fridman *et al.*, Plasma Process. Polym. **5** (2008) 503.

2 Y. Sakiyama and D. B. Graves, J. Phys. D **39** (2006) 3644.

3 Y. Sakiyama and D. B. Graves, J. Phys. D **41** (2008) 095204.

4 J. Goree *et al.*, J. Phys. D **39** (2006) 3479.

5 Y. Sakiyama and D. B. Graves, Plasma Sources Sci. Technol. **18** (2009) 025022.

9:40am **PS-FrM5 A Novel Way of using Plasma to Sterilize Objects for Use in Medical, Food or Pharmaceutical Applications**, ***N.B. Koster***, *F.P. Wieringa, R. Koops*, TNO Science and Industry, Netherlands

From literature it is known that plasma is capable of sterilizing objects. A number of the great advantages of plasma sterilization is that it is relatively cool and that it also has a cleaning action besides the sterilisation process. A disadvantage of plasma sterilization is that for a good process the object has to be placed in a reactor and after the process is completed the object has to be packed in an enclosure and sealed. This is a possible source of cross contamination due to handling and exposure to the environment. We will present a novel way of using plasma's to sterilize an object without this disadvantage. This process is called Plasma in a Bag (PiB) and has the benefit that the object is packed and sealed from the environment before the process starts and requires no handling after the sterilization process has finished. Also the way of packing enables the user to see that the enclosure is still intact and that the integrity of the object remains valid even after a long shelf life. We will show results on the efficiency of the process for several pathogens at different plasma conditions. This new process enables the use of new materials and electronics for medical applications or can replace a number of existing sterilisation techniques.

10:00am **PS-FrM6 Patterned Growth of Cells and Biomolecules using a Microplasma Printing System**, *E. Yildirim-Ayan,* Drexel University, ***D. Pappas***, Army Research Laboratory

A versatile system called *micro-plasma integrated cell/biomolecule printing system* is described. This system enables the creation of patterned cells/biomolecules on various substrates without using any masks, master stamps or chemical treatments. The system operation is based on the integration of two techniques, namely microplasma patterning and cell/biomolecule printing. In microplasma patterning, an atmospheric pressure low-temperature microplasma is generated with a dielectric barrier discharge (DBD) plasma setup consisting of a micro-second pulsed power supply and electrode system. Through *micro-plasma integrated cell/biomolecule printing system,* we can create chemically and physically

predesigned micropatterns and print the cells/biomolecules on designed pattern with precise spatial positioning.

In this study, the authors patterned mouse osteoblast cells on ultra high molecular weight polyethylene films. An O_2/He mixture was used as the working gas for the ignition of a micron-sized discharge. The microplasma nozzle with a tip of 30 µm was navigated on a straight line with a 2mm/s speed to create the micropattern. The physicochemical properties of the microplasma patterned surface were examined by Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS). The SEM data showed that the dynamic microplasma treatment results in an increase of the surface roughness. The surface morphology was changed along the microplasma treated line while the rest of the substrate remained unaffected. The XPS data showed that the atomic concentration of oxygen increased from 5% for the as-received polyethylene film to 18% for the center of the microplasma treated line. Following the micropatterning, mouse osteoblast cells were deposited uniformly on the substrate to determine the effect of microplasma patterning on cell attachment. The biological characterization has been done by live/dead assay where mouse osteoblast cells were labeled and imaged using fluorescence microscopy. The data showed the attachment and survival of the cells strictly along the plasma activated line. With these observations, it is viable to print the cells and dictate their shapes in predetermined locations and arrays through *micro-plasma integrated cell/biomolecule printing system*.

10:20am **PS-FrM7 How Does the Chemical Equilibrium in the Vaporous Phase Influence the Surface Properties of Poly-Parylenes?**, *T.H.T. Huber, F. Schamberger,* ***G. Franz***, Munich University of Applied Sciences, Germany

The properties of deposited polymeric films strongly depend on the density and the state of excitation of the species in the vaporous phase which determine the degree of consecutive reaction paths covering the bandwidth between volume polymerization and surface polymerization. According to Yasuda, the former reaction mainly causes roughened fine-grain deposits, whereas smooth and shiny layers can be generated easily by the latter one [1]. For chemical vapor deposition, the main parameters are gas flow, number density (degree of rarefaction) and gaseous temperature which are extended by a row of additional parameters in plasma-activated processes, beginning with the (absorbed) plasma power and terminating with the delicate parameters obtained by diagnostic tools. These changes in the reaction mechanism were extensively studied for the biocompatible molecule parylene (*p*-xylylene) which is already deposited on stents for tribological purposes and is intended to cover the inner surface of artificial bladders [2]. We investigated the deposition two types of pure parylene (type N: non-substituted, and type C: substituted by one Cl atom), diluted with different amounts of argon, and a reactive alternative by adding oxygen [3]. The *in-situ* methods are energy-dispersive mass spectrometry and Langmuir probe analysis which have been correlated with *ex-post* measurements of the film quality: contact angle (surface energy) and the morphology, but most prominent the content of the aromatic species in the volume of the layer which goes down not unexpected with growing plasma power. Adding oxygen opens the window to a hydrophilic response of the surface. With the knowledge of densities of the dimeric precursor, the monomeric species, and the electron density, we modeled the chemical equilibrium of dissociation, and from the density of the aromatic compounds in the layer, we could follow the track of "safe" polymerization and could also describe the ranges for volume polymerization and surface polymerization [4].

[1] H. Yasuda: *Plasma polymerization*, Academic Press, New York (1985)

[2] G. Franz, F. Rauter, S. Dribinskiy, JVSTA, to be published

[3 K.G. Pruden, K. Sinclair; J. Polymer Sci. **A41**, 1486 (2003)

[4] G. Kokkoris, V. Constantoudis, P. Angelikopoulos, G. Boulousis, E. Gogolides; Phys. Rev. **B76**, 193405 (2007)

10:40am **PS-FrM8 Synthesis of Polystyrene and Sulfonated Polystyrene Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition**, ***D. Merche***, Université Libre de Bruxelles (ULB), Belgium, *C. Poleunis, P. Bertrand,* Université Catholique de Louvain (UCL), Belgium, *M. Sferrazza, F. Reniers*, Université Libre de Bruxelles (ULB), Belgium

Thin coatings of pp-PS and pp-sulfonated PS were synthesized by "Plasma Enhanced Chemical Vapour Deposition" (PECVD) in a home-built "Dielectric Barrier Discharge" (DBD) system near atmospheric pressure. Styrene (C_8H_8) and trifluoromethane sulfonic acid (CF_3SO_3H) monomers were used as precursors and were introduced in the discharge using a flux of Ar or He. An atmospheric RF plasma torch was also used for PS deposits. It consists of two closely spaced perforated metallic electrodes. The process gas is Ar. The precursor (styrene vapour) was introduced into the plasma downstream of the electrodes (afterglow). The polymers were deposited on various substrates (PTFE, HDPE, stainless steel, glass, and silicon wafer) and were characterized by FTIR, XPS, SSIMS, WCA, AFM and optical microscopy. The plasma phase was studied by OES.

The pp-sulfonated PS films obtained by plasma copolymerization could present interesting properties as electrolyte membrane for miniaturized fuel cell applications (Polymer Electrolyte Membrane Fuel Cell- PEMFC) using H_2 or CH_3OH (Direct Methanol Fuel Cell-DMFC). CF_3SO_3H allows introduce the sulfonic acid groups for proton conductivity in the membrane whereas the styrene constitutes the backbone of the membrane.

The major features that characterize PS are present in the FTIR, XPS and SSIMS spectra, although some differences between pp-PS films and their conventionally polymerized counterparts are observed (like oxygenation during or after deposition due to the atmosphere environment, branching, degree of cross-linking, and unsaturations). According to the WCA and XPS results, the pp-PS films deposited by the RF plasma torch (placed in a plexiglass chamber) are more oxygenated than those deposited by the DBD operated in a much more controlled atmosphere [1]. The chemical structure of the deposited coatings was investigated by FTIR and TOF-SSIMS as a function of the nature of the carrier gas. The pp-PS films synthesized in the presence of Ar (for both processes) exhibit more branching, more unsaturations, a higher degree of cross-linking, and a lower density of aromaticity than pp-PS synthesized with He as the main plasma gas.

The influence of the nature of the carrier gas, and of the discharge voltage and the ratio of the partial pressures of the monomers on the sulfonic content (therefore on the degree of fragmentation of the CF_3SO_3H monomer) for both carrier gases was investigated for pp-PS sulfonated by XPS, SSIMS and FTIR.

[1] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, *IEEE Transactions on Plasma Science* (2009), Under Press, Available online on http://www.ieeetps.org/

11:00am **PS-FrM9 Functionalization of Wood Surfaces in the Afterglow of an Atmospheric Pressure Dielectric Barrier Discharge**, ***J. Prégent***, Université de Montréal, Canada, *F. Busnel,* Université Laval, Canada, *V. Blanchard,* FPInnovations-Division Forintek, Canada, *L. Stafford*, Université de Montréal, Canada

The use of wood products in architectural or exterior applications is often limited by the short durability of these products and the fast deterioration of their appearance. Several waterborne coatings aimed at preserving the wood properties have been developed but these coatings are often characterized by poor adhesion on wood surfaces. To improve adhesion, we investigated modification of the surface properties of wood samples following their exposition to the afterglow of an atmospheric pressure dielectric barrier discharge in N_2/O_2 mixtures. The surface energy divided into a dispersive (non-polar) part, γ_{DS}, and a polar part, γ_{PS}, was determined by means of contact angles measurements. For polar sugar maple samples, γ_{PS} decreased from 78.5 mJ/m^2 before treatment to 59.0 mJ/m^2 after N_2 plasma exposure. γ_{PS} further decreased with the introduction of O_2, reached a minimum value of 31.2 mJ/m^2 at 85%N_2-15%O_2, and then increased until it reached its untreated value in a pure O_2 plasma. The dispersive component showed the opposite behavior, going from 3.3 mJ/m^2 before treatment to 24.4 mJ/m^2 after exposure to the 85%N_2-15%O_2 plasma. On the other hand, no modification was observed for black spruce, probably because untreated samples already had a large dispersive component. Optical emission spectroscopy (OES) was used to understand the change in plasma properties leading to the observed variation of γ_{PS} and γ_{DS}. The gas temperature determined using the second positive system of N_2 ($C^3\Pi_u$ v'=0 – $B^3\Pi_g$ v''=2) was 320 ± 20 K and showed no trend with O_2 concentration, thus ruling out variations due to thermal effects. Significant NO ($A^2\Sigma^+$ - $X^2\Pi$) emission in the 225-305 nm range was observed in pure N_2 plasmas. However, these bands disappeared with the introduction of O_2, indicating that UV photons are not the prominent species driving the observed decrease in surface polarity. We also observed a strong increase of the N_2^+ ($B^3\Sigma_u$ v'=0 - $X^2\Sigma_g^+$ v''=0) to N_2 ($C^3\Pi_u$ v'=0 – $B^3\Pi_g$ v''=2) bandhead intensity ratio with increasing O_2 concentration. Such behavior is usually ascribed to an increase signature of the early afterglow and thus to an increase in the erosion rate of polymer surfaces [1]. In pure N_2 plasmas, one expects N grafting to form nitrogen-containg groups which are likely to promote non-polar bonding [2]. As only a moderate decrease of γ_{PS} was observed in pure N_2 and no change was observed in pure O_2, it is believed that a combination of N grafting and surface erosion by oxygen atoms is required to achieve maximum modification of the surface polarity.

[1] M.K. Boudam et al., J. Phys D. **40**, 1694 (2007)

[2] S. Vallon et al., J. Adhes. Sci. Technol. **10**, 1287 (1996)

11:20am **PS-FrM10 Combination of Bio-template and Ultimate Top-down Etching Processes for Defect-free, High Density, Size-controlled and Excellent Uniform Si-Nanostructure for Ideal Quantum Effect Devices**, ***M. Igarashi***, *C. Huang,* Tohoku University, Japan, *M. Takeguchi,* NIMS, Japan, *S. Horita,* JAIST, Japan, *Y. Uraoka, T. Fuyuki,* NAIST, Japan, *I. Yamashita,* Panasonic Co., Ltd. and NAIST, Japan, *S. Samukawa*, Tohoku University, Japan

Nanometer-scale structures such as quantum dots (QDs) have been widely studied because they have potential applications to the development of quantum effect devices, such as single electron transistors, quantum dot lasers and quantum dot solar cells. To realize quantum dots, the fabrication of defect-free, size-controlled and uniform sub-10-nm-scale structures is needed. However, it is difficult for conventional optical lithography and plasma etching processes to satisfy these requirements.

In this study, we proposed a novel nanofabrication process for the fabrication of nanostructures, which combines a biomaterial template, radical etching and neutral beam etching (NBE). We fabricated silicon nanodisks (disk-shaped silicon nanostructures with diameters of about 10 nm on a very thin silicon oxide film) by using a ferritin iron core as etching mask and Cl NBE. Additionally, we succeeded in precisely controlling the nanodisk diameter by using surface treatment of NF_3 gas + hydrogen radicals (NF_3 treatment). The surface oxide thickness and its removal conditions greatly affected the fabricated nanodisk diameter. It was notable that the coulomb staircases of nanodisk structures were obtained with a conducting AFM probe at room temperature. The successful fabrication of Si nanodisk should be attributed to the defect-free etching process that involved our neutral beam. Our new process is very useful to fabricate defect-free and size-controlled nanostructure for ideal quantum effect devices.

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Chen, S.: PS1-WeM11, **22**
Chen, Z.: PS-ThP5, **38**
Chen, Z.Y.: PS2-ThA4, **35**
Cheng, H.-Y.: PS1-ThM11, 29
Chevolleau, T.: PS1-MoM10, 2; PS1-MoM11, 2; PS1-MoM5, 1
Chiang, W.-H.: PS2-TuM1, 9
Chistyakov, R.: SE2-MoM4, 4
Cho, S.H.: PS-TuP2, 16
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Choi, S.I.: PS-TuP15, 18
Choudhary, G.K.: PS1-ThA9, **34**; PS-TuA12, 13; PS-TuA9, 13
Chu, C.: PS1-MoM8, 2
Chung, T.-Y.: PS-TuA10, 13; PS-TuA9, **13**
Cloud, A.N.: SE2-MoM11, **5**
Cohen, S.: PS2+TF-WeM3, 23
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Creatore, M.: PS2-TuM5, 10; PS-TuP10, 17
Cremer, R.: SE2-MoM1, **4**
Cuddy, M.: PS1-ThA4, **33**
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Darlak, A.: PS1-MoM9, 2; PS-TuP3, 16
Dasaka, R.K.: PS1-ThM11, 29
David, T.: PS1-MoM10, 2; PS1-MoM11, 2; PS1-MoM5, 1
De Graeve, I.: PS2+TF-WeM1, 22
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de Vries, H.: PS2-TuM5, 10
Degendt, S.: PS2-ThA11, 36
Dekker, J.: PS2+MN-WeA2, **26**
Diao, L.: PS1-TuM11, **8**
Dictus, D.: PS2-ThA11, **36**
Dilonardo, E.: PS2+TF-WeM6, 23
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Ding, G.: PS-TuP1, **16**
Donnelly, V.M.: PS1-ThA6, **33**; PS2-ThA4, 35; PS2-ThM10, 31; PS2-TuM9, 10
Dorf, L.: PS1-WeA9, 26; PS1-WeM5, **21**; PS2-ThM1, 30
Douhard, B.: PS2+TF-WeM1, 22
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Dürr, M.: SS1+PS+TF+AS+NS-TuA12, **15**
Dufour, T.: PS2-TuM11, 11
Dunin-Borkowski, R.E.: SS1+PS+TF+AS+NS-TuA7, 14
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Economou, D.J.: PS1-WeA1, **25**; PS2-ThA4, 35; PS2-TuM9, 10
Eichhorn, L.: PS2+PV-MoM4, **3**
Ellingboe, A.R.: PS2+PV-MoM11, 4; PS2-ThM4, **30**; PS-ThP6, 39
Enache, I.: PS2-TuM3, 9
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Eppler, A.: PS1-TuM10, 8
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Fairbrother, H.: SS1+PS+TF+AS+NS-TuA1, **14**
Fanelli, F.: PS2-TuM2, **9**
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Feurprier, Y.: PS1-MoM8, 2
Fisher, E.R.: PS1-ThA4, 33; PS1-ThM12, 29; PS2+TF-WeM9, 24
Flauta, R.E.: PS1-WeM4, 21; SE2-MoM11, 5
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Franquet, A.: PS-TuA7, 12
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Fukasawa, M.: PS1-TuM9, 8
Fukuda, S.: PS2+MN-WeA3, 26; PS2-ThA2, 35
Funk, M.: PS2-ThA4, 35; PS2-ThM2, 30; PS2-ThM9, 31; PS-ThP17, 40
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Gaman, C.: PS2+PV-MoM11, 4; PS2-ThM4, 30
Gao, F.: PS2+MN-WeA1, **26**; PS2+MN-WeA2, 26
Gates, S.M.: PS2+TF-WeM3, 23
Gatilova, L.: PS2-ThA8, 36
Gebhardt, C.: SS1+PS+TF+AS+NS-TuA12, 15
Gherardi, N.: PS2-TuM3, **9**
Giet, J.M.: PS-FrM2, 42
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Goeckner, M.: PS2-TuM11, 11; PS-TuA3, **12**
Gorham, J.: SS1+PS+TF+AS+NS-TuA1, 14
Goto, T.: PS2-ThM12, **32**
Gouraud, P.: PS1-TuM5, 7
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Guillermet, M.: PS1-MoM10, 2
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Hamaguchi, S.: PS1-ThM10, 29; PS1-TuM9, 8
Hansen, T.A.R.: PS1-ThA3, **33**
Hansen, T.W.: SS1+PS+TF+AS+NS-TuA7, 14
Hargrove, W.F.: PS2-TuM6, 10
Harrison, S.: PS-ThP2, **38**
Hayashi, H.: PS1-MoM1, 1; PS-TuP7, 17
Helmersson, U.: SE2-MoM6, 5
Henry, F.: PS2+TF-WeM10, **24**
Heo, W.: PS2+MN-WeA9, 27
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Hirao, T.: PS2-ThM6, 31
Hoang, J.: PS1-WeA4, 25
Hoban, J.A.: PS1-WeM9, 22
Hollenstein, Ch.: PS2+PV-MoM9, 4
Hong, S.P.: PS2-ThM5, 30; PS-ThP4, **38**
Hooke, W.M.: PS2-TuM6, 10
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Hori, M.: PS-ThP11, 39; PS-TuP20, 19; PS-TuP7, 17
Horita, S.: PS-FrM10, 44
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Ito, T.: PS1-ThM10, 29; PS1-TuM9, **8**
Iwashita, S.: PS2+TF-WeM5, **23**; PS-TuP21, 19
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Kaminatsui, T.: PS-TuP7, 17
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Kato, K.: PS-TuA11, 13
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Kelber, J.: PS1-MoM3, **1**
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Kim, H.S.: PS-TuP2, 16
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Kim, J.S.: PS2+MN-WeA9, 27; PS-TuP4, 16
Kim, K.N.: PS2-ThM5, 30; PS-ThP4, 38
Kim, S.G.: PS-TuP15, 18
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Kimura, Y.: PS2-ThM6, 31
Kinder, R.: PS2+TF-WeM12, 24
Kintaka, H.: PS1-TuM6, **8**
Kitajima, T.: PS-TuP18, 19
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Koster, N.B.: PS-FrM5, **42**
Kothnur, P.: PS2+TF-WeM12, **24**
Koyama, K.: PS-TuA11, **13**
Krupczak, E.: SS1+PS+TF+AS+NS-TuA11, 15
Kuboi, N.: PS1-TuM9, 8
Kudlacek, P.: PS1-ThM5, **28**
Kunnen, E.: PS-TuA7, **12**
Kurihara, K.: PS1-MoM1, **1**
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Lahr, D.L.: PS-TuP9, 17
Lange, C.: PS1-WeM2, **21**
Lange, M.: SE2-MoM10, **5**
Lau, S.: SS1+PS+TF+AS+NS-TuA11, 15
Lauer, J.L.: PS1-ThA10, **34**
Layet, J.M.: PS1-ThA1, 33
Lee, C.: PS1-TuM10, 8; PS-TuP1, 16
Lee, H.S.: PS-ThP14, 40
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Lee, J.Y.: PS1-TuM1, 7
Lee, M.S.: PS-TuP2, **16**
Lee, N.-E.: PS2+MN-WeA9, 27; PS-TuP4, **16**; PS-TuP5, **16**
Lee, S.H.: PS1-WeA11, **26**; PS-TuP15, 18
Lee, S.K.: PS2+MN-WeA9, 27; PS-TuP2, 16
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Lin, C.-H.: PS-ThP7, 39
Lin, J.: SE2-MoM4, 4
Lin, T.: PS-TuA12, 13
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Lovascio, S.: PS2-TuM2, 9
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Lymberopoulos, D.: PS1-TuM1, 7
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Maechler, L.: PS2-TuM3, 9
Maeda, S.: PS-TuA11, 13
Makabe, T.: PS-TuP18, 19
Manandhar, S.: PS1-MoM3, 1
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Marchelli, A.: PS-ThP16, 40
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Martin, A.R.: PS2-TuM6, 10
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Martin, S.: PS2+TF-WeM6, 23
Massines, F.: PS2-TuM3, 9
Matsui, T.: PS2+PV-MoM5, 3
Matsumoto, Y.: PS1-ThM10, 29
Matsuoka, T.: PS2-ThM12, 32
Matsuzaki, H.: PS2+TF-WeM5, 23; PS-TuP20, 19
Mattei, S.: PS2-ThM10, 31
Meng, L.: PS1-WeM4, **21**
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Merche, D.: PS-FrM8, **43**
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Michna, T.: PS2-ThM4, 30; PS-ThP6, **39**
Mignot, Y.: PS1-MoM8, 2
Milella, A.: PS2+TF-WeM6, **23**
Miller, D.: PS1-ThM11, 29
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Miura, N.: PS2-TuM10, **10**
Miyata, H.: PS2+TF-WeM5, 23; PS-TuP21, 19
Mochiki, H.: PS2+MN-WeA4, **27**
Momose, H.: PS-TuA11, 13
Moon, Ch.S.: PS-ThP11, **39**
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Mori, T.: PS1-TuM6, 8
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Naudé, N.: PS2-TuM3, 9
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Nisol, B.: PS-TuP16, **18**
Noh, T.H.: PS-TuP15, 18
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Nozawa, T.: PS1-TuM6, 8; PS2-ThM9, 31; PS-ThP17, 40
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Oehrlein, G.S.: PS-TuA10, 13; PS-TuA12, 13; PS-TuA9, 13
O'Farrell, D.: PS2+PV-MoM11, **4**; PS2-ThM4, 30
Oh, D.: SS1+PS+TF+AS+NS-TuA3, 14
Oh, J.S.: PS2+PV-MoM2, 3; PS-TuP11, **17**
O'Hara, N.: PS2-ThM4, 30
Ohiwa, T.: PS2+MN-WeA7, 27; PS-TuP7, 17
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Ohta, H.: PS1-ThA8, 34
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Okamoto, S.: PS2+MN-WeA4, 27
Ono, K.: PS1-ThA8, 34; PS1-ThM9, 29
Orlando, T.M.: SS1+PS+TF+AS+NS-TuA3, **14**
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Paffen, R.M.J.: PS2-TuM5, 10
Palumbo, F.: PS2+TF-WeM6, 23
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Pappas, D.: PS-FrM6, **42**
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Park, J.B.: PS1-TuM4, 7; PS2+PV-MoM2, **3**; PS-TuP11, 17
Park, J.S.: PS2+MN-WeA9, 27
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Patel, V.: PS2+TF-WeM3, 23
Paterson, A.: PS1-TuM10, **8**
Patz, R.: PS1-MoM9, 2; PS-TuP3, 16
Peeters, F.J.J.: PS2+PV-MoM8, 4; PS-TuP10, **17**
Pender, J.: PS1-MoM9, 2; PS-TuP3, 16
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Poleunis, C.: PS-FrM8, 43; PS-TuP16, 18
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Premkumar, A.P.: PS2-TuM5, 10

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Ramaswamy, K.: PS1-TuM1, 7; PS1-WeM5, 21
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Rego, R.: PS-TuP10, 17
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Roberg, J.: PS1-WeM3, 21
Rohde, S.L.: SE2-MoM11, 5
Rosenberg, S.: SS1+PS+TF+AS+NS-TuA1, 14
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Ruzic, D.N.: PS1-WeM4, 21; PS1-WeM9, 22; SE2-MoM11, 5
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Sakurai, N.: PS2+MN-WeA7, 27
Samukawa, S.: PS1-ThM3, **28**; PS2+MN-WeA3, 26; PS2-ThA2, 35; PS2-ThM11, 31; PS-FrM10, 44; PS-TuA11, 13
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Sankarapandian, M.: PS1-MoM8, 2
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Sasaki, M.: PS1-TuM6, 8
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Schiesko, L.: PS1-ThA1, 33
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Schröder, H.: SS1+PS+TF+AS+NS-TuA12, 15
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Schwarz, B.: PS-TuP1, 16
Seki, N.: PS2-ThM12, 32
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