Spectroscopic Ellipsometry Focus Topic
Room: 19 - Session EL+TF+AS+EM+SS+PS+EN+NM-MoM

Spectroscopic Ellipsometry for Photovoltaics and Semiconductor Manufacturing
Moderator: M. Creatore, Eindhoven University of Technology, the Netherlands, H. Wormeester, MESA+ Institute for Nanotechnology, Univeristy of Twente, Enschede, The Netherlands

8:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM1 Multichannel Spectroscopic Ellipsometry: Applications in I-III-VI_2 Thin Film Photovoltaics**, ***R.W. Collins***, *D. Attygalle, P. Aryal, P. Pradhan, N.J. Podraza,* University of Toledo*, V. Ranjan, S. Marsillac*, Old Dominion University **INVITED**

Multichannel spectroscopic ellipsometry (SE) has been applied successfully as an in situ, real time tool for optimizing, monitoring, and controlling multi-stage deposition processes in various thin film photovoltaics (PV) technologies. A particularly challenging process optimization problem involves the thermal co-evaporation of individual elements of Cu, In, Ga, and Se in a three-stage process, which has proven to produce high quality $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) materials and high performance PV devices. This three-stage process provides a high level of flexibility in determining the phase, composition, and microstructure of the film, but also generates greater challenges in run-to-run reproducibility of the optimized process. Information extracted from real time SE measurements includes the evolution of the bulk layer and one or more surface layer thicknesses, as well as layer dielectric functions. The layer dielectric functions can be analyzed further to extract the phase and alloy compositions and the defect density or grain size, which can assist in understanding the fabrication process, in optimizing solar cells, and ultimately in monitoring and controlling the optimized process for improved reproducibility. In this study, the focus is on analysis of ellipsometric (ψ, Δ) spectra acquired by real time SE in order to characterize (i) the structural and compositional evolution in $(In,Ga)_2Se_3$ film growth from In, Ga, and Se fluxes in the first stage, (ii) the transition from Cu-poor to Cu-rich CIGS at the end of the second stage, which occurs under Cu and Se fluxes, and (iii) the transition from Cu-rich to the desired Cu-poor CIGS, which defines the end of the third and final stage, and occurs under a second application of In, Ga, and Se fluxes. After the transition from Cu-poor to Cu-rich material in the second stage, a $Cu_{2-x}Se$ phase near the surface of the bulk layer is tracked. In the Cu-rich to Cu-poor transition, this $Cu_{2-x}Se$ phase has fully reacted with In, Ga, and Se to form CIGS. Studies using a standard Mo substrate and 2 µm thick CIGS for solar cells have also revealed features in the (ψ, Δ) spectra characteristic of the anticipated changes in the near surface phase composition as established by detailed modeling on thinner and smoother films. Although careful analysis of real time SE is expected to provide quantitative information on the surface properties and their evolution in this case of solar cells, control of the deposition has been successful simply by monitoring real time changes in the ellipsometric (ψ,Δ) spectra.

9:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM3 Contribution of Plasma Generated Nanoparticles to the Growth of Microcrystalline Silicon Deposited from SiF_4/H_2/Argon Gas Mixtures**, ***J.-C. Dornstetter***, *S. Kasouit, J.-F. Besnier,* Total S.a, France*, P. Roca i Cabarrocas*, LPICM-CNRS, Ecole Polytechnique, France

Despite the low fabrication cost of thin film silicon solar modules, this type of technology remains non competitive in main stream markets because of the high BOS costs, due to the low energy conversion efficiency of this type of modules (~10%).We have recently shown that microcrystalline silicon films deposited using SiF_4/H_2/Argon RF capacitive plasmas have excellent structural and transport properties, compared to films deposited using conventional SiH_4/H_2 mixtures, allowing for a very good carrier collection, even for thick cells, and Voc values of 0.55 V, without device optimization, thus opening up the path for the realization of high performance solar cells. However, little is known so far about the growth mechanism of this type of materials and the reason for such interesting properties.Studies of silicon thin films deposition from SiF_4/H_2 mixes, under conditions different from ours, suggested that the growth is due to the deposition of SiF_2 radicals, followed by the abstraction of fluorine by hydrogen. Previous work within our group has also shown that deposition occurs only when particles are present in the plasma, and that growth starts from crystallites without any amorphous phase.We present here a systematic study of the growth of microcrystalline films, together with the composition of nanoparticles attracted by thermophoresis to cold traps located both on the walls of the plasma chamber and in the fore line as a function of deposition conditions. The composition of the deposit on the traps is found to be amorphous at low power/ low hydrogen conditions and becomes crystalline when either of them increases. This correlates well with an increase in atomic hydrogen concentration in the plasma, as estimated by actinometry. The crystalline fraction of the deposited film was measured using in-situ ellipsometry and was found to correlate with the composition of the deposit on the cold traps. Deposition rate is drastically reduced when a water cooled trap is installed on the walls of the plasma chamber, and switches off at high H_2 flow rates. Under these conditions, TEM and AFM images, show that at the initial stages of the growth the film is constituted of sparse, hexagonal crystalline particles, having sizes on the order of few tens of nanometers. We interpret the data above as a result of plasma-generated nanocrystals being a significant contribution to the deposited film. This may explain the excellent electronic properties of the films, as the particles are formed in the bulk of the plasma region, free from energetic ions bombardment. We will correlate the structural properties and the film growth mechanisms to the properties of solar cells.

9:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM4 Multichannel Spectroscopic Ellipsometry for CdTe Photovoltaics: from Materials and Interfaces to Full-Scale Modules**, ***P. Koirala****, J. Chen, X. Tan, N.J. Podraza,* The University of Toledo*, S. Marsillac,* Old Dominion University*, R.W. Collins*, The University of Toledo

Real time spectroscopic ellipsometry (RTSE) has been implemented in studies of the evolution of the semiconductor structural and optical properties during sputter deposition of thin film polycrystalline CdS/CdTe solar cells on transparent conducting oxide (TCO) coated glass substrates. Analysis of the real time optical spectra collected during CdS/CdTe deposition requires an optical property database as a function of measurement temperature for all substrate components. These include not only soda lime glass, but also an SiO_2 layer and three different SnO_2 layers. We report optical functions parameterized versus temperature for the glass substrate and its overlayers starting from room temperature and ending at elevated temperature above which the semiconductor layers are deposited. In fact, such a database has additional applications for on-line, through-the-glass monitoring applications of coated glass at elevated temperature. In the RTSE studies, knowledge of the temperature dependent optical functions of the substrate components enables an accurate substrate temperature determination before the onset of deposition and is critical for accurate extraction of the semiconductor layer optical properties. We implement RTSE to study the filling process of the surface roughness modulations on the top-most SnO_2 substrate layer and modification of the optical properties of this layer. This modification is further studied post-deposition by infrared spectroscopic ellipsometry. In addition to providing information on interface formation to the substrate during film growth, RTSE also provides information on the bulk layer CdS growth, its surface roughness evolution, as well as overlying CdTe interface formation and bulk layer growth. Information from RTSE at a single point during solar cell stack deposition assists in the development of a model that can be used for mapping the completed cell stack properties, which can then be correlated with device performance. Independent non-uniformities in the layers over the full area of the cell stack enable optimization of cell performance combinatorially.

9:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM5 Determination of Electronic Band Gaps from Optical Spectra**, ***R.A. Synowicki***, J.A. Woollam Co., Inc.

The band gap of a material Eg is defined theoretically as the lowest energy for electronic transition from the valence to conduction bands in a solid. For an ideal material free of defects this is the photon energy or wavelength where the optical properties change from transparent to absorbing. However, real materials contain defects which cause absorption to begin below the band gap (i.e. the Urbach Tail) making determination of the true band gap position difficult. For example, in a solar cell the measured absorption edge represents the onset of transitions first due to defects, then from band to band. Empirical methods used to determine the band gap in real materials with defects include the Tauc plot and the Mott-Davis plot. More theoretical mathematical dispersion models such as the Tauc-Lorentz, Cody-Lorentz, and Herzinger-Johs models have been developed which include an adjustable band gap parameter. The various plots and dispersion model methods will be discussed and applied to different materials measured optically via spectroscopic ellipsometry, intensity transmission, reflection, absorption, or a combination of these methods.

10:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM6 Optical Modeling of Plasma-Deposited ZnO: Extended Drude and its Physical Interpretation**, ***H.C.M. Knoops***, *M.V. Ponomarev, J.W. Weber, N. Leick, B.W.H. van de Loo, Y.G. Melese, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, the Netherlands

High-quality transparent conductive oxides such as ZnO are important due to their electrical and optical properties. To improve these properties the responsible physical processes have to be understood. Traditionally, charge-carrier-scattering processes are investigated by combining morphology data and Hall measurements. This contribution discusses the extensive optical modeling of plasma-deposited ZnO and how its interpretation directly provides insight into the relevant charge-carrier-scattering processes at different length scales. The interpretation is generalized to the concept of frequency-dependent resistivity, which is used to explain the applicability of different Drude models.

Thin films (50-1000 nm) of Al-doped and undoped ZnO were deposited using an expanding thermal plasma MOCVD process.[1] Conditions of high pressure and high diethyl zinc flow allowed for dense films with low electrical resistivities (e.g., 4×10^{-4} Ω cm at 300 nm). The films were analyzed with variable-angle spectroscopic ellipsometry (SE) (0.75 – 5.0 eV), FTIR reflection spectroscopy (0.04 – 0.86 eV), Four-point-probe (FPP), and Hall measurements.

The SE and FTIR data were combined and fitted with classical and extended Drude[2] models. The high intensity of the Drude in the FTIR range resulted in a high sensitivity with which the carrier concentration and mobility could even be determined for thin (~40 nm) undoped ZnO films. An extended Drude model was needed to correctly model the SE energy range, which was explained by the dominance of ionized impurity scattering and a reduction of this scattering for higher photon energies. The grain-boundary-scattering mobility could be determined by the difference between optical and Hall mobilities.[3] When combined with FPP results, the effective mobility can be determined from these optical techniques without the use of Hall measurements. The optical response above the band gap was modeled by a PSEMI or Tauc-Lorentz oscillator model, where a broadening and shift of the transition was seen for increasing carrier concentration.[4]

These insights and a generalized view of electron scattering in ZnO at different length scales will be presented.

1. Ponomarev et al., *J. Appl. Phys.* **Submitted** (2012)

2. Ehrmann and Reineke-Koch, *Thin Solid Films* **519**, 1475 (2010)

3. Steinhauser et al., *Appl. Phys. Lett.* **90**, 142107 (2007)

4. Fujiwara and Kondo, *Phys. Rev. B* **71**, 075109 (2005)

10:40am **EL+TF+AS+EM+SS+PS+EN+NM-MoM8 The Ellipsometric Response of Single-Crystal Silicon to Doping**, ***H.G. Tompkins***, Consultant

The current wisdom is that for ellipsometry in the UV-vis-NIR spectral range, doping of single-crystal silicon can be ignored. We study the ellipsometric response of silicon doped with arsenic at various levels. We also studied the response after implant (before activation) and after the activation (anneal). We find that for samples implanted with 1E18 atoms/cm3, the single-crystal silicon was not amorphized. Implants of 2E19 atoms/cm3 and higher left an amorphous layer on the surface of the wafer the thickness of which was about the depth of the implant. Activation of the sample implanted with 2E19 atoms/cm3 returned the sample to single-crystal silicon and the ellipsometric response in the UV-vis-near_IR is essentially that of undoped silicon. However, the response in the mid-IR is that the extinction coefficient is no longer zero. For samples implanted with 2.5E20 atoms/cm3 and greater, annealing did not return the UV-vis-near_IR ellipsometric response to that of single-crystal silicon. Although this amount of other material (arsenic) is still less that about one tenth of one percent, our conjecture is that the microstructure simply could not be returned to that of a single crystal. As with the lower doped sample, the mid-IR spectral region showed significant increase in the extinction coefficient.

11:00am **EL+TF+AS+EM+SS+PS+EN+NM-MoM9 The Effect of Stress on the Optical Properties Semiconductor Films**, ***A.C. Diebold***, *G.R. Muthinti, M. Medikonda, T.N. Adam,* College of Nanoscale Science and Engineering, University at Albany, *A. Reznicek, B. Doris*, IBM Research at Albany Nanotech

Here we review the impact of stress on the complex dielectric function of semiconductor films measured using spectroscopic ellipsometry. Two relevant examples of stressed semiconductor layers are pseudomorphic epitaxial layers fabricated during semiconductor manufacturing and strained silicon on insulator (sSOI) wafers. Stress is known to shift the energies of direct gap critical point transitions in semiconductors. The biaxial stress in pseudomorphic films grown on silicon wafers can be as high as that used during opto-elastic studies of bulk semiconductors. The amount of stress in un-relaxed, pseudomorphic films of $Si_{1-x}Ge_x$ on Si (100) reaches 1 GPa for alloys with 20% Ge and is more than 3 GPa for films with > 50% Ge. The bi-axial stress in sSOI is typically ~1 GPa. An elastic theory approach for the effect of strain on the k*p determined band structure and optical transition energy is well known. Both low shear stress and high shear stress approximations can apply to the shift in transition energy depending on the magnitude of the spin orbit splitting energy vs the magnitude of the shear stress. Until recently it was difficult to obtain sets of samples that test both approximations. Here we discuss results from our recent study of pseudomorphic films of $Si_{1-x}Ge_x$ on Si (100) from x= 0.05 to 0.75 which covers both low and high shear regimes. We also present our recent study of the dielectric function of thinned sSOI which illustrates the impact of stress on the optical transitions for the Si layer on sSOI. All of these samples are examples of new materials being used in semiconductor research. The results of this study are directly transferred into cleanroom spectroscopic ellipsometry systems used for process control during manufacturing.

11:20am **EL+TF+AS+EM+SS+PS+EN+NM-MoM10 Numerical Ellipsometry: Spectroscopic n-k Plane Analysis of Thin Films Growing on Unknown Layered Substrates**, ***F.K. Urban***, *D. Barton*, Florida International University

Spectroscopic ellipsometry measurements on thin films commonly make use of prior knowledge of the structure and optical properties of the underlying substrate. However, imprecision in substrate statistics propagates into the solution for the film of interest. Thus it is more accurate to have a method for solving for film properties which simultaneously obtains whatever is needed about the substrate. And it makes solutions possible whether or not book data or previous substrate solutions are available. In this work we apply Complex Analysis in the n-k plane to achieve solutions employing the well-know reflection equations. The method is carried out at each measured wavelength and does not necessitate an *a-priori* assumption of optical property dependencies on wavelength. The mean square error has been improved by many orders of magnitude, a selected limit of 10^{-14} as opposed to 1 to 30 or so for least squares. Thus the full accuracy of the ellipsometer is now available for more accurate measurements of film thickness and optical properties. The method requires six measurements during growth. The first is used to determine the relationship between Rp and Rs at the film-substrate interface. The following four are used to uniquely determine the values of Rp, Rs, and film n, k, and d. The final measurement confirms the unique solution. Suitability of the model is tested by comparing measurements at two of more wavelengths for self consistency. Results for n and k of the growing film are examined across the measurement spectrum in comparison with parameterizations in common use.

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+EM+NS+PS+SS+TF-MoM

Graphene Growth
Moderator: M. Spencer, Cornell University, V.D. Wheeler, U.S. Naval Research Laboratory

8:20am **GR+EM+NS+PS+SS+TF-MoM1 Synthesis Ingredients Enabling Low Noise Epitaxial Graphene Applications**, ***D.K. Gaskill,*** *L.O. Nyakiti, V.D. Wheeler,* U.S. Naval Research Lab*, A. Nath,* George Mason Univ.*, V.K. Nagareddy,* Newcastle University, UK*, R.L. Myers-Ward, N.Y. Garces, S.C. Hernández, S.G. Walton,* U.S. Naval Research Lab*, M.V. Rao,* George Mason Univ.*, A.B. Horsfall,* Newcastle Univ., UK*, C.R. Eddy, Jr.,* U.S. Naval Research Lab, *J.S. Moon*, HRL Labs LLC

Sensors made from graphene flakes have demonstrated single molecule detection [Schedin *et al*., Nat Mat **6**, 652 (2007)]; this ultra-sensitivity is likely due to the high crystalline quality of the graphene and the associated relative lack of defects that give rise to noise. The low noise nature of high quality graphene should also facilitate other applications, e.g., low-noise amplifiers. Combined with the unique ambipolar property of graphene field effect transistors (FETs), the low noise character of graphene would significantly advance the performance of frequency multipliers, mixers and high-speed radiometers. To exploit these applications, high quality, reproducible wafer-scale epitaxial graphene (EG) with minimal thickness variations and defects are essential requirements. Here, crucial graphene synthesis elements required to achieve the wafer-scale quality goal are described. Understanding the effect of substrate misorientation as well as hydrogen etch and Si sublimation conditions for graphene synthesis on the (0001) SiC surface is essential to achieve improved and reproducible wafer-scale graphene quality. For example, the impact of processing factors such as temperature control, laminar gas flow and substrate rotation on large area EG uniformity are described using examples created in an Aixtron SiC

epitaxy reactor. In addition, managing SiC step formation on the nominal (0001) orientation is significant for achieving uniform EG thickness on terraces and to minimize additional growth at the step edges; this is illustrated using data from atomic force microscopy and scanning electron microscopy images in combination with Raman spectroscopy maps and x-ray photoelectron spectroscopy analysis. Managing step formation combined with optimal growth leads to the suppression of the Raman defect "D" band confirming minimal grain boundaries and defects, which are additional sources of electronic noise. Lastly, contactless Lehighton resistivity maps of 75 mm wafers are used to illustrate the overall uniformity of optimally synthesized graphene as well as to show the re-sistance state-of-the-art, with individual wafers exhibiting about a ±3% relative variation. Examples of the impact of this synthesis approach on chemical sensors devices and FETs will be shown, each exhibiting 1/f noise behavior down to 1 Hz and possessing noise spectral densities similar to reports from exfoliated graphene. Hence, careful control of EG formation across the wafer results in improved quality which subsequently leads to the reduction or elimination of additional noise sources from graphene defects that would then adversely affect device performance.

8:40am **GR+EM+NS+PS+SS+TF-MoM2 Growth of Graphene by Catalytic Decomposition of Ethylene on Cu(100) and Cu(111) With and Without Oxygen Predosing**, ***Z.R. Robinson***, *P. Tyagi, T. Mowll, C.A. Ventrice, Jr.,* University at Albany- SUNY*, K. Clark, A.-P. Li*, Oak Ridge National Laboratory

Graphene growth on Cu substrates has become one of the most promising techniques for the mass production of graphene, and therefore significant effort has been put into developing growth conditions that lead to large area, defect and grain boundary free graphene films. One key consideration is the influence that the underlying copper substrate has on the growth of the graphene. In order to study this, graphene growth on Cu(100) and Cu(111) was carried out in a UHV system. The samples were heated using an oxygen series button heater. The hydrocarbon pressure was measured using a capacitive manometer instead of an ion gauge, which could cause dissociation of the hydrocarbon molecules. Initially, it was found that annealing the crystals to 900 °C resulted in impurity segregation at the surface. Several cycles of sputtering at 600 °C were required to remove all bulk impurities so that the surface remained clean even after annealing to 900 °C. Initial attempts to grow graphene by annealing each crystal to temperatures as high as 900 °C in UHV, followed by backfilling the chamber with up to 5 x 10^{-3} torr of C_2H_4 did not result in graphene formation. It was found that by first backfilling the chamber with C_2H_4 and then raising the temperature from 25 °C to 800 °C, graphene growth could be achieved. A four-domain epitaxial overlayer is observed for the Cu(100) surface. Pre-dosing the Cu(100) with oxygen at 300 °C, which forms a saturation coverage of chemisorbed oxygen, was found to result in a 2-domain graphene overlayer using similar growth conditions. A study of the effect of oxygen pre-dosing on the growth of graphene on Cu(111) has been initiated.

9:00am **GR+EM+NS+PS+SS+TF-MoM3 Impact of Growth Parameters on Uniformity of Epitaxial Graphene**, ***L.O. Nyakiti***, *V.D. Wheeler, R.L. Myers-Ward, J.C. Culbertson,* U.S. Naval Research Laboratory*, A. Nath,* George Mason University*, N.Y. Garces,* U.S. Naval Research Laboratory*, J. Howe,* Oak Ridge National Laboratory*, C.R. Eddy, Jr., D.K. Gaskill*, U.S. Naval Research Laboratory

Epitaxial graphene (EG) offers a facile method for attaining large area graphene for device applications. Since wafer uniformity and thickness control is vital, a systematic study of the parameters affecting the EG growth process was performed and the optimal conditions for obtaining uniform morphology and high electronic quality were determined. EG was synthesized in a low pressure Ar flowing ambient on 8x8mm^2 6H-SiC(0001) substrates that were offcut 0.8° from the basal plane, using an Aixtron VP508 reactor. The samples were placed on a rotating ~100 mm diameter susceptor and excellent EG layer uniformity and run-to-run reproducibility were obtained. The investigation focused upon the critical synthesis parameters of temperature (T) (1520-1660°C) and time (t) (15-60 min), an *in-situ* H_2 etch conditions (1520-1600°C for 10-30min). Morphology, layer thickness, chemical analysis, and strain variations across the samples were characterized using electron microscopy, AFM, XPS and µ-Raman spectroscopy. Large-area van der Pauw Hall effect was performed to quantify the graphene mobility (µ), and carrier density. Results show that growth T and t had the most significant impact on EG electronic and morphological properties. For example, synthesis at 1660°C for 30min resulted in 4-8 monolayers (ML) and a step-bunched morphology with high concentration of wrinkles originating from the step-edge and pinned at the nearest terrace edge. Other morphological features were pits primarily located at the step edges having a depth ~20nm and density 6.4x10^6 cm^{-2}. In contrast, EG synthesis at 1520°C for 30min results in uniform ML coverage along the terrace width that is devoid of pits and wrinkles. Mobility was found to have a drastic dependence on graphene thickness. Under optimal conditions, 1-2 ML were obtained and µ as high as 1240 $cm^2V^{-1}s^{-1}$ was achieved; in contrast, for EG with >2 ML µ ~ 550 $cm^2V^{-1}s^{-1}$, presumably due to interlayer interaction and electronic screening. XPS C1s and Raman 2D spectra of EG grown on substrates after undergoing *in-situ* H_2 etch at different times did not show shifts in peak position/intensity suggesting lack of etch time dependence on EG electronic or structural quality. Yet etch conditions affect the final morphology, as EG synthesis performed after an *in-situ* H_2 etch at 1600°C resulted in step-bunched morphology with step heights 5-10nm, whereas, substrates etched at 1520°C had EG with step-heights 10-15nm. In addition other growth parameters investigated were found to be of secondary importance, including: Ar pressure, flow rates, and sample cool down conditions.

9:20am **GR+EM+NS+PS+SS+TF-MoM4 Uniform Epitaxial Growth of Charge Neutral Quasi-Free-Standing Monolayer Graphene on a 6H-SiC(0001) Surface by Combination of Metal Silicidation and Intercalation**, ***H. Shin***, *I. Song, C.-Y. Park, J.R. Ahn*, Sungkyunkwan University, Republic of Korea

Intrinsic high mobility of graphene are much reduced in graphene devices by various factors. Two critical factors degrading mobility are uniformity in an atomic structure such as number of a layer and an interaction with a substrate. Recently Shuai-Hua Ji *et al*. reported quantitatively that conductivity is much reduced by one sixth when electrons pass through a boundary between monolayer and bilayer graphene at a step edge in comparison to conductivity of monolayer graphene. This suggests that uniformity of number of graphene layer is a more crucial factor than expected. In particular, in epitaxial graphene on SiC, the uniformity of number of layer is an intrinsic and serious problem because Si is more rapidly sublimated near a step edge in the formation of epitaxial graphene by thermal evaporation of Si and, subsequently, epitaxial graphene with different layers coexists intrinsically on a terrace. Another factor degrading mobility is an interaction between graphene and a substrate. In epitaxial graphene, the interaction was reduced by intercalation of metal or molecule such as H, F, and Au between graphene and a substrate, which results in quasi freestanding graphene. Various charge neutral quasi freestanding graphene has been reported, but the charge neutrality was found at an optimal coverage of an intercalated element and annealing temperature. This makes it difficult to achieve spatially homogeneous charge neutrality of quasi freestanding graphene, and a method with a broad range of coverage and temperature is demanded. We demonstrate that charge neutral quasi freestanding monolayer graphene can be grown uniformly without coexistence of a buffer layer and a bilayer graphene which limit mobility of epitaxial monolayer graphene. Because coexistence of two different phases is inevitable on a SiC surface, uniform monolayer graphene was produced based on two different phases, a Si-rich phase and a C-rich phase called a buffer. Pd was deposited on both the Si-rich and C-rich phases and annealed up to 900°C. The Si-rich phase produced Pd silicide and charge neural quasi freestanding monolay graphene was produced on the Pd silicide while, on the C-rich phase, Pd was intercalated between the buffer layer and SiC resulting in charge neutral quasi freestanding monolayer graphene, where the quasi freestanding monolayer graphene on two difference regions was connected atomically. The combination of Si silicidation and intercalation result in uniform charge neutral quasi freestanding uniform monolayer on a SiC surface, where the electronic and atomic structures were observed using angle-resolved photoemission spectroscopy and scanning tunneling microscopy.

9:40am **GR+EM+NS+PS+SS+TF-MoM5 Epitaxial Graphene on Ir(111) - A Playground for the Fabrication of Graphene Hybrid Materials**, ***T.W. Michely***, Universität zu Köln, Germany **INVITED**

Carefully optimizing the growth of graphene on Ir(111) yields a virtually defect free, weakly bound epitaxial monolayer ranging from quantum dot sizes to macroscopic extension. In the talk I will show how this system can be used to construct new types of graphene based materials. Specifically, patterned adsorption of transition metals results in dense cluster arrays with exciting magnetic and catalytic properties. Intercalation underneath the graphene allows one to manipulate the properties of graphene itself, e.g. its ability to adsorb atoms and molecules as well as its magnetism.

10:40am **GR+EM+NS+PS+SS+TF-MoM8 Graphene Growth Studied with LEEM, PEEM, EELS, ARPES, MEIS, and STM**, ***R.M. Tromp***, *J.B. Hannon, M.W. Copel, S.-H. Ji, F.M. Ross*, IBM T.J. Watson Research Center **INVITED**

We have studied the growth of graphene on a variety of substrates, including SiC (both Si and C terminated), polycrystalline Cu and Ni foils, as well as single-crystal Ni foils. Low Energy Electron Microscopy (LEEM) and Photo Electron Emission Microscopy (PEEM) offer the unique opportunity to follow the growth in real time, as it proceeds at high temperature, and in the presence of processing gases such as disilane (for

growth on SiC) or ethylene (for growth on the metal substrates). Low Energy Electron Diffraction (LEED) allows us to determine crystallographic orientations as well as atomic structure of areas well below a micrometer in extent. Information on electronic structure can be obtained from the plasmon loss features using Electron Energy Loss Spectroscopy (EELS), or from Angle Resolved Photo Electron Spectroscopy (ARPES). These spectroscopic experiments are carried out in the LEEM/PEEM microscope using an in-line energy filter with which energy and angle resolved analysis of the electrons can be performed on selected areas. Finally, to obtain information on the layer-by-layer evolution of the graphene films, particularly on SiC, we have used isotope sensitive Medium Energy Ion Scattering (MEIS), to follow the growth by thermal decomposition of ^{12}C vs ^{13}C graphene monolayers from a three-bilayer thick $Si^{13}C$ homoepitaxial film grown on a SiC substrate. Taken together, these results provide a comprehensive view of the growth of graphene films. In this talk, we will review the most salient results of these studies, and their relevance to the use of graphene films for electronic applications. To address the latter, we will discuss the results of three-probe STM experiments in which we measured the excess resistivity of a graphene sheet as it crosses an atomic step of the underlying substrate.

11:20am **GR+EM+NS+PS+SS+TF-MoM10 Spatial Confinement of Epitaxy of Graphene on Microfabricated SiC to Suppress Thickness Variation**, ***H. Fukidome***, *T. Ide, H. Handa,* RIEC, Tohoku Univ., Japan, *Y. Kawai,* Tohoku Univ., Japan, *F. Fromm,* Univ. Erlange-Nürnberg, Germany, *M. Kotsugi, T. Ohkouchi,* JASRI/SPring-8, Japan, *H. Miyashita,* Tohoku Univ., Japan, *Y. Enta,* Hirosaki Univ., Japan, *T. Kinoshita,* JASRI/SPring-8, Japan, *Th. Seyller,* Univ. Erlange-Nürnberg, Germany, *M. Suemitsu*, RIEC, Tohoku Univ., Japan

Epitaxial graphene on SiC (EG) is promising owing to a capability to produce high-quality film on a wafer scale [1]. One of the remaining issues is microscopic thickness variation of EG near surface steps, which induces variations in its electronic properties and device characteristics. To suppress the variation, spatial confinement of surface reactions is effective. The spatial confinement using substrate microfabrication, for instance homoepitaxy and sublimation on microfabricated Si substrates, can induce self-ordering of steps, and even produce step-free surfaces [2]. The spatial confinement is therefore anticipated effective to obtain EG without the thickness variation.

We have for this reason applied the spatial confinement to the epitaxy of graphene on 6H-SiC(0001). For the spatial confinement, 6H-SiC(0001) substrates were microfabricated by using electron beam lithography and fast atomic beam etching using sulfur hexafluoride [3, 4]. Epitaxial graphene on the microfabricated 6H-SiC(0001) substrates was obtained by annealing at 1923 K in Ar ambience [2]. It is verified by using low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) that step-free SiC surface and EG without thickness variation can be formed on smaller patterns [4]. This result clearly demonstrate that the spatially confinement is effective for the epitaxy of graphene on SiC. Furthermore, Raman spectroscopy and LEEM reveals that the spatial confinement can suppress the fluctuations of the electronic properties, e.g. (unintentional) doping in EG [4].

In conclusion, we have demonstrated that the spatial confinement of EG is effective to control both structural and electronic properties. This novel technique can boost the development of electronic devices based on EG.

[References]

[1] K. V. Emstev et al., Nature Mater. 8 (2009) 203.

[2] Y. Homma et al., Jpn. J. Appl. Phys. 35 (1996) L241.

[3] T. Ide et al., accepted for the publication in Jpn. J. Appl. Phys.

[4] H. Fukidome et al., submitted.

11:40am **GR+EM+NS+PS+SS+TF-MoM11 Three-Dimensional Graphene Architecture Growth and Its Facile Transfer to Three-Dimensional Substrates**, ***J.-H. Park***, Sungkyunkwan University, Republic of Korea, *H.-J. Shin, J.Y. Choi,* Samsung Advanced Institute of Technology, Republic of Korea, *J.R. Ahn*, Sungkyunkwan University, Republic of Korea

Recent development of large area graphene synthesis on metal layer by chemical vapor deposition (CVD) or epitaxial growth on silicon carbide (SiC) opened the possibility for applications such as transparent electrodes for ITO replacement. For instance, graphene has been demonstrated for use in a liquid crystal display (LCD) and/or organic light emitting diode (OLED) test cell as a bottom electrode. However, the actual device, e.g., an active-matrix (AM) LCD, operates by switching individual elements of a display, using a thin-film transistor (TFT) for each pixel. Here, the pixel electrode of a display should extend down to the transistor's source or drain, thereby making contact with a via hole, which demands that a three-dimensional (3D) architecture electrode be deposited on a flat surface as well as its side walls. Although large-area graphene growth can be applied for a wide range of applications, 3D graphene architecture growth has not been realized for actual devices due to the original limitation of planar graphene growth. Herein, we demonstrate for the first time 3D graphene architecture growth and its facile transfer to a planar and/or 3D substrate. To prevent agglomeration of nano-scale metal catalyst by the CVD process, we chose a SiC system. Graphene, a few layers thick, was epitaxially grown on a pre-patterned SiC substrate with nano-size thickness which was produced by photolithography and dry etching. Graphene on a vertical facet of the SiC pattern with a few-hundred nanometers in height was perfectly prepared using this approach, contrary to the CVD method. Furthermore, we suggest the use of a facile transfer method of graphene on SiC to a SiO2 substrate using thermal release tape after hydrogen intercalation. In spite of the troublesome transfer issue of SiC, the geometry of the 3D graphene was perfectly transferred onto the planar SiO2 as well as the 3D SiO2 structure. In other words, the 3D graphene architecture was maintained as a floating cap structure on planar SiO2 and the vertical facet of the 3D SiO2 structure was well covered. Moreover, the graphene bottom layer without a 3D cap and the inverted bowl structure in the 3D graphene architecture were selectivly transferred by controlling intercalation and pressure. These approaches could provide a beneficial method for preparing a 3D graphene architecture as well as for modifying the ordered structure to be utilized in real devices.

Plasma Science and Technology
Room: 24 - Session PS+EM-MoM

Atmospheric Plasma Processing and Micro Plasmas
Moderator: S.G. Walton, Naval Research Laboratory

8:20am **PS+EM-MoM1 Plasma Science and Applications in the Spatial Realm Below 1 mm: Recent Advances in Microcavity/Microchannel Plasmas**, ***J.G. Eden***, University of Illinois at Urbana Champaign **INVITED**

The last decade has witnessed the rapid emergence of microcavity plasmas, a new subfield of plasma science and technology that pursues the fundamental physics and applications of low temperature, nonequilibrium plasma confined in at least one dimension to nominally < 1 mm. By melding plasma science with photolithography and other micro/nanofabrication techniques adapted from the integrated circuits and materials science communities, it has become possible to observe plasma behavior and realize electronic/photonic/chemical devices that were inaccessible previously. With all due respect to Captain Kirk, plasmas are now able "to go where no [plasma] has gone before." This presentation will highlight recent advances in microcavity plasma science, such as the realization of plasma confined to < 3 µm. Interfacing a gas phase (e^- – ion) plasma with an e^- – h^+ plasma in a semiconductor to yield an n^+pn plasma bipolar junction transistor will be described. A new form of thin, flat lighting ("lighting tiles") available in sheets as large as 900 cm^2 in area will be demonstrated, and massively-parallel plasmachemical processing of gases/vapors in arrays of microchannel plasmas will be described.

9:00am **PS+EM-MoM3 Development and Limitations of Microplasma Arrays on Silicon Operating in DC**, ***R. Dussart***, *M. Kulsreshath, L. Schwaederle, V. Felix, P. Lefaucheux, O. Aubry, T. Tillocher, S. Sozias,* GREMI - Polytech Orleans/CNRS, France, *L.J. Overzet*, University of Texas at Dallas

Arrays of microreactors built from silicon wafers in clean room facilities were first proposed and developed about ten years ago by G. Eden's team [1]. They consist of Micro Hollow Cathode Discharges (MHCD) operating in parallel in DC or in AC. One of the remarkable properties of these MHCDs relies on the fact that they can operate in DC, in a stable regime at atmospheric pressure, without evolving to an arc regime [2]. Potential applications of these new technological devices are numerous and include different domains such as lighting, detection, local treatments, sensors, lab on chip, treatment and micromachining processing, instrumentation… In this paper, we will focus on DC operation of microdischarges working in helium or in argon. The microreactor geometry was investigated to achieve the best results in terms of life time and ignition. Although we were able to ignite up to 1024 microdischarges (100 µm diameter holes), we observed many spikes on the current waveform, which indicate that microplasmas are not so stable. The quite short life time of our microdevices which varies from few minutes to few hours could be linked to these spikes, which actually cause significant damages. Taking into account our observations by Scanning Electron Microscope, our optical characterization and our electrical measurements, we propose a mechanism explaining the appearance of the damages, which shorten the lifetime of our

microdischarges. Finally, we will give some indications to delay the damage mechanisms and to increase the life time of the microplasma arrays.

References

[1] J G Eden, S-J Park, N P Ostrom, S T McCain, C J Wagner, B A Vojak, J Chen, C Liu, P von Allmen, F Zenhausern, D J Sadler, C Jensen, D L Wilcox and J J Ewing, J. Phys. D: Appl. Phys. 36 2869–2877 (2003)

[2] K. H. Schoenbach, R. Verhappen, T. Tessnow, P. F. Peterkin, W. Byszewski, Appl. Phys. Lett. 68, 13 (1996)

9:20am **PS+EM-MoM4 A Foldable Microplasma-Generation Device on a Paper Substrate Operating under Atmospheric Pressure***, **Y.J. Yang**, J.H. Tsai, Y.C. Liao, Y.W. Lu, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

The fabrication of plasma generating devices on paper substrates is presented. The device was fabricated using a screen print process. Stable helium plasmas were ignited in two parallel electrodes with a gap of 237 to 710 µm by a DC power source. When the plasma was ignited with a 0.2 µL salt solution droplet with trace amount of metallic elements applied to the discharge gap, clear metallic emission lines emanated from the plasma. The result suggests that this paper-based device can be used in analytical applications. We demonstrate that a stable helium plasma can be sustained when the substrate is flat, rolled, and folded along various orientations. Microarrays were also fabricated on paper substrates. Stable array of discharges can be ignited by an AC power source with a frequency between 50 Hz to 10 kHz. Preliminary results show that a 10*10 discharge array can be ignited under different atmospheres such as argon, helium, and air by properly adjusting the parameters. This work was supported by National Science Council of Taiwan, the Republic of China (100-2628-E-002-012 and 101-3113-E-002-002).

9:40am **PS+EM-MoM5 Cold Atmospheric Microplasma Arrays for Processing of Flexible Materials***, **J. Hopwood**, A. Hoskinson, C. Wu, N. Miura*, Tufts University **INVITED**

Microplasmas offer a pathway to atmospheric pressure plasma processing using low-temperature, low-cost substrates. Unlike arc and torch technologies, the atmospheric microplasma typically operates near room temperature. Corona discharges share this distinction, but modern microplasma devices produce electron densities that are several orders of magnitude greater than the corona. The combination of low gas temperature and high electron density suggests that a unique process window exists for deposition, etching, and surface modification of flexible materials at atmospheric pressure. In this lecture, we describe the plasma physics of a steady-state microplasma excited by 1 GHz microwave power. Spatially resolved laser diode absorption, imaging spectroscopy, and electrical probe measurements show that the individual microdischarge has an intense inner core surrounded by a cooler region that is rich in metastable atoms. These physical insights are combined with data from deposition experiments using acetylene mixed with a helium gas flow. High densities of electrons and energetic species produced by steady-state microplasmas are believed to be crucial to quality film formation at one atmosphere. Finally, we explore scaling the microplasma toward roll coating geometries. Linear arrays of microplasmas are excited from a single microwave power source through the use of resonant energy sharing. This technique allows over 100 microplasmas to operate in parallel without the usual problem of instabilities induced by ionization overheating and negative differential discharge resistance. This work was supported in part by the U.S. Department of Energy under award No. DE-SC0001923 and by the National Science Foundation under Grant No. CBET-0755761.

10:40am **PS+EM-MoM8 Nucleation of Nanodiamond Clusters at Ambient Pressure via Microplasma Synthesis***, **A. Kumar**, P.A. Lin, A. Xue, R.M. Sankaran*, Case Western Reserve University

Since their discovery, nanodiamonds have been an active area of research due to their unique size, chemical stability, high thermal conductivity, and biocompatibility.[1] Nanodiamonds have been detected in outer space (meteorites, interstellar dust) and synthetically produced by high pressure/high temperature (HPHT) and detonation processes. In addition to their potential technological use, the formation of nanodiamond is of great scientific interest. While bulk graphite is more stable than bulk diamond at lower pressures and temperatures (e.g. ambient conditions), recent modeling has suggested that nanometer-sized particles of diamond-phase carbon could be thermodynamically favored at these same conditions as a result of surface energy considerations.[2]

Previously, microplasmas have been shown to be capable of nucleating high-purity nanometer-sized metal nanoparticles from vapor precursors.[3] Here, we present a study of nanodiamond synthesis at atmospheric pressure using a similar microplasma process. Ethanol vapor was used as a carbon precursor for the nucleation of carbon clusters. Aerosol measurements confirm that carbon clusters less than 6 nm in mean diameter are nucleated in the microplasma. *In situ* optical emission spectroscopy (OES) indicates the presence of C_2 dimers and atomic H species which have been linked to diamond nucleation. The collected product is characterized by several techniques including micro Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM). Results confirm the presence of nanodiamond with uniform sizes of *ca.* 3 nm in diameter and crystal structures corresponding to known phases of diamond. The synthesis of nanodiamond at low pressure may allow new technologies to be realized, and help explain their formation in extraterrestrial material.

1. V. N. Mochalin *et al.*,“The properties and applications of nanodiamonds”, *Nat. Nanotech.* **7**, 11 (2012).

2. P. Badziag *et al.*, “ Nanometre-sized diamonds are more stable than graphite”, *Nature* **343**, 244 (1990).

3. A. Kumar *et al.*, “New insights into plasma-assisted dissociation of organometallic vapors for gas-phase synthesis of metal nanoparticles”, *Plasma Proc. Polym.*, in review.

11:00am **PS+EM-MoM9 Atmospheric Pressure Plasma Effects on the Adhesive Bonding Properties of Stainless Steel and Epoxy Composites***, **T.S. Williams**, H. Yu, P. Yeh, J. Yang, R.F. Hicks*, University of California, Los Angeles

An atmospheric pressure helium and oxygen plasma has been used for the surface preparation of 410 stainless steel and carbon-fiber epoxy laminates prior to bonding them together. Lap shear results for stainless steel coupons and carbon-fiber epoxy laminates demonstrated an 80% and a 150% increase in bond strength, respectively, after plasma activation. Following 7 days of aging, wedge crack extension tests revealed a crack extension length of 7.0 mm and 2.5 mm for the untreated and plasma activated steel. The untreated stainless steel had 30% cohesive failure compared to 97% for steel activated with the plasma. Surface analysis by X-ray photoelectron spectroscopy showed that carbonaceous contamination was removed by plasma treatment, and specific functional groups, e.g. carboxylic acids, were formed on the surface. These functional groups promoted strong chemical bonding to the epoxy film adhesive. Atmospheric pressure plasmas are an attractive alternative to abrasion techniques for surface preparation prior to bonding. The process is easily automated, does not damage the materials, and has no environmental, health and safety concerns.

11:20am **PS+EM-MoM10 Numerical Simulation of Gas Heating in a Capacitively Coupled Microcell Plasma at Atmospheric Pressure***, **T. Yagisawa**, T. Makabe*, Keio University, Japan

A microcell plasma at atmospheric pressure has been widely investigated. One of the biggest advantages is in the capability to produce a small-size and high-density plasma, broadening a range of applications such as nano-material synthesis, light sources, biomaterial processing, green technology and so on. With decreasing the size of the reactor, the ratio of volume to surface area also decreases. Under these circumstances, the contribution of the wall surface to the loss of charged and neutral particles becomes much larger. The energy is accumulated in the plasma in the form of a thermal energy by the interaction between energetic ions and gas molecules and the ion impact on the wall. Therefore, the effects of local heating of gas molecule on the plasma structure is of great inportance particularlly in a microcell plasma at high pressure.

In this study, the two-dimensional (2D) structure of a capacitively coupled microcell plasma (CCP) driven at radio frequency (13.56 MHz) with the power of ~4.7 W cm^{-3} is numerically investigated in a sealed cylindricals chamber at atmospheric pressure. Pure argon is considered as a parent gas molecule, where electron, Ar^+, Ar_2^+ and long-lived metastable atom (Ar^m) are traced in the simulation. In order to discuss the effects of local gas heating, the governing system consisting of a coupled set of models is developed: a neutral transport model including the gas temperature T_g, a conventional plasma model in gas phase, as well as a heat conduction model in solid phase. Large amount of metastable atom ~10^{14} cm^{-3} makes huge influence on the plasma structure via stepwise ionization process caused by low energy electrons (~4.3 eV), as well as metastable pooling. The temperature dependence of the thermal conductivity (~ $T_g^{1/2}$) of argon is considered and the result is compared with that of constant thermal conductivity. The local peak of gas temperature T_g ~ 600 K appears due to the Joule heating by energetic ions in the sheath region in front of the powered electrode, resulting in the local reduction of gas density $N_g(r)$ under the constant gas pressure. Taking the gas heating into account, electron density increases by the enhancement of reduced field $E/N_g(r)$. In addition, electron density distribution slightly expands toward the radial direction.

11:40am **PS+EM-MoM11 Reactions at the Interface of Plasmas and Aqueous Electrodes: Identifying the Role of Electrons**, *M. Witzke,* Case Western Reserve University*, P. Rumbach, D.B. Go,* University of Notre Dame, ***R.M. Sankaran***, Case Western Reserve University

Plasmas formed at the surface of or inside liquids have been of historical interest for the potential to mediate electrochemical reactions with gaseous species.[1] Recently, there has been technological interest in plasma/liquid systems for a wide range of applications including nanomaterials synthesis, water treatment, and medicine. However, the nature of reactions at the plasma/liquid interface remains poorly understood. Specifically, since plasmas are a source of electrons, ions, UV light, and radicals, it has been difficult to isolate and identify the role of the various species on reactions that occur in the liquid phase.

Here, we present evidence of electrolytic reactions at the plasma/liquid interface. Experiments were carried out with a non-thermal, atmospheric-pressure, direct-current microplasma jet formed at the surface of an aqueous electrolyte. The plasma was operated as the cathode with a Pt foil immersed in solution as the anode. To isolate the role of electrons, we selected model electrolytic reactions such as the conversion of ferricyanide [$Fe(CN)_6^{3-}$] to ferrocyanide [$Fe(CN)_6^{4-}$] which can be easily monitored by UV-vis absorbance spectroscopy.[2] Cyclic voltammetry was performed to verify that ferricyanide was not dissociated. Alternatively, using acidic solutions, hydrogen gas was detected by mass spectrometry, indicating that protons (H^+) are electrochemically reduced by the plasma.[3] Overall, these results reveal the significant role electrons can play in plasma/liquid systems.

1. J. Gubkin, *Ann. Phys. Chem. N. F.* **32,** 114 (1887).

2. M. Witzke *et al.*, *J. Am. Chem. Soc.* **133**, 17582 (2011).

3. M. Witzke *et al.*, submitted.

Plasma Science and Technology
Room: 25 - Session PS-MoM

Advanced FEOL/Gate Etching 1
Moderator: L. Diao, Mattson Technology

8:20am **PS-MoM1 Selective Etching of Spacer with Pulsing in Inductively Coupled Plasmas for FinFET Devices**, *B. Zhou, M. Titus, P. Friddle, M. Robson,* ***G. Upadhyaya****, G. Kamarthy,* Lam Research Corp*, S. Kanakasabapathy, E. Franke*, IBM Corp

The transition to 14 nm technology node has introduced an architectural shift from traditional planar devices to complex three-dimensional FinFET structures. A primary etch challenge for making FinFET devices is that of spacer etch wherein the topography of the FinFET devices requires the fin surface (Si) to withstand substantial over-etch in order to remove the spacer on the fin sidewalls. Typical targets for this etch comprises of < 1nm Si recess, good spacer profile fidelity, complete spacer removal on fin sidewalls and < 2nm spacer CD loss. With conventional etch methodologies, the process window for achieving these targets is narrow due to competing deposition and etch species that simultaneously co-exist in the plasma. Simply lowering the electron temperature or lowering the ion energy is not a solution since there is a tradeoff between spacer CD loss and Si recess. In this presentation, we will demonstrate that by using pulsing, the deposition and etch phases can be separated thereby yielding a wide process window and breaking the tradeoff to enable FinFET spacer etch. Various pulsing schemes will be contrasted with conventional continuous mode operation along with a discussion of the compatibility of the pulsed spacer process with downstream integration.

8:40am **PS-MoM2 Evaluation of Novel Spacer Etch Processes using a New Gas**, ***S. Engelmann****, E.A. Joseph, N.C.M. Fuller, W.S. Graham, E.M. Sikorski,* IBM T.J. Watson Research Center*, M. Nakamura, G. Matsuura,* Zeon Chemicals L.P.*, H. Matsumoto, A. Itou, T. Suzuki*, Zeon Corporation

The spacer etch process is a very critical element in the CMOS device process flow as it ensures and enables the electrical isolation of Source/Drain and Gate regions. We observed that during conventional spacer processes, very little difference in plasma polymer deposition onto the respective substrates could be noted. [1] A successful Nitride Spacer process was rather facilitated by a silicon etch process that was selective to oxide, where excess oxidation lead to a conversion of Silicon to Silicon oxide. This also means that the etch rates of the Nitride are limited by the simultaneous oxidation of the nitride. A potential solution to overcome this limitation would be to control the etch rate by polymer thickness, similar to high selectivity oxide etching. An evaluation of this approach has yielded similar results as the general etch mechanism proposed by Standaert et al. [2] A novel etch chemistry was also evaluated that enables a different etch mechanism that cannot be described by the general model.

The impact of this novel mechanism on spacer etch processes was evaluated for both, capacitive and inductive discharges. We furthermore evaluated the impact of this novel process on planar and non-planar device structures. The novel gas chemistry has also been evaluated to enable an oxygen free spacer process. We found that the lateral spacer loss can be eliminated and that Si loss can be effectively reduced by employing the novel process. The SiN footing can be effectively reduced by fine-tuning the ion/neutral ratio of the plasma discharge. The best results to date from a PDSOI 22nm testsite have yielded an SOI loss of about 2nm which is able to maintain all SiN on the gate sidewall while keeping the HM loss to about 4nm and reducing the SiN foot to less than 3nm.

[1] S. Engelmann et al., AVS 58th Int. Symp. & Exhibit. (2011)

[2] M. Schaepkens et al., J. Vac. Sci. Technol. A 17, 26 (1999)

9:00am **PS-MoM3 Anisotropic and Selective Etching of Novel Multifunctional Materials**, ***J.P. Chang***, University of California, Los Angeles **INVITED**

The introduction of new and improved materials into silicon based integrated circuits is a major contributor in the recent decade to enable the scaling of circuit density and performance in analog, logic, and memory devices. Many new materials, such as complex metal oxides, magnetic materials and phase change materials, are much harder to pattern, thus pose significant challenges to the design and selection of plasma etching chemistries. This talk focuses on understanding the plasma-surface interaction and reaction kinetics, offers an unique approach in that thermodynamics analysis guides the selection of gas-phase chemistry, and establishes a kinetics-based model containing salient attributes of the etch process. The significant gain deriving from this unique approach is the ability to assess a large array of materials, which possess different properties that dictates a careful balance between etch anisotropy and selectivity. Both theoretical and experimental results from recent research will be discussed using complex metal oxides and magnetic materials are model systems.

9:40am **PS-MoM5 High Selective Etching of SiN Based Material Over Si and SiO_2 using Evanescent Microwave Plasma for FINFET Spacer Applications**, ***A. Raley****, A. Ranjan, H. Kintaka, B. Messer, T. Mori, K. Kumar, P. Biolsi,* Tokyo Electron Technology Center, America, LLC*, A. Inada,* Renesas Electronics*, R. Jung, S. Kanakasabapathy*, International Business Machines – Research Group

For smaller than 22nm technology node devices, a FinFET (3-D) gate structure is needed to reduce gate leakage, decrease power consumption, increase drive current and control short channel effects. FinFET gate spacer etching presents challenges for conventional RIE process, since it requires highly anisotropic and selective etching of Silicon Nitride over Si/SiO2. Microwave power was delivered through radial line slot antenna generating high density evanescent microwave plasma. High density evanescent microwave plasmawith low self-bias at the wafer enables a highly selective and anisotropic etching of spacer. The bulk electron energy distribution determines the gas phase reaction rates that generate various radicals and ionic species. The etchant, passivant and ion flux to the wafer can be controlled by the energy distribution of Bulk electrons (T_e). T_e can be tuned in by adjusting the microwave power. High SiN selectivity over Si and SiO2 was achieved on blanket as well as patterned wafer using the evanescent microwave plasma etcher. In general, selectivity is achieved by controlling the polymer layer difference over SiN/Si/SiO2. The difference of pattern wafer/blanket wafer etch rates/selectivities can be explained by differences in transport of by ions and radicals through high aspect ratio features. The effects of loading of SiN, Si and resist materials on etch rates and selectivity will be reviewed.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Research Alliance Teams in Albany, NY 12222. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities

10:00am **PS-MoM6 Highly Selective and Controllable Si_3N_4 Etching to Si and SiO_2 for sub-22-nm Gate Spacer using CF_3 Neutral Beam with O_2 and H_2**, ***D. Nakayama****, A. Wada, T. Kubota,* Tohoku University, Japan*, M. Haass, R.L. Bruce, R.M. Martin, N.C.M. Fuller,* IBM TJ Watson Research Center*, S. Samukawa*, Tohoku University, Japan

Silicon nitride is used as a gate sidewall spacer for aggressively scaled complementary metal-oxide-semiconductor (CMOS) devices because of their high thermal stability and excellent insulating property. Therefore, silicon nitride (Si_3N_4) etching (patterning) is one of the critical processes in

sub-22-nm-CMOS device fabrication. During the patterning of the silicon nitride spacer film, damage to the Si surface typically occurs, resulting in silicon (Si) and Si dioxide (SiO_2) recess in the source/drain and shallow trench isolation (STI) respective regions. Additionally, loss of spacer film close to the top of the gate structure can occur during the excessive "over etch" necessary to enable a manufacturable process. The advent of non-planar device geometries only exacerbates the aforementioned challenges. Hence, extremely high selectivity of silicon nitride to both Si and SiO_2 is extremely critical.

We developed an alternative etching process to solve these problems using a "damage-free" neutral beam (NB) etching process. A typical NB apparatus consists of plasma and process chambers that are separated by a carbon aperture. The carbon aperture can effectively neutralize the charged particles and eliminate irradiation of UV photons from plasma when the plasma passes through it. Therefore, etching can proceed without any UV-induced damage caused by charged particles or high-energy photons from the plasma.

In this study, we proposed neutral beam etching using a new gas chemistry of CF_3I in addition with oxygen (O_2) and hydrogen (H_2) gases for the sidewall spacer etching process. By using CF_3I, we can ensure that an energetic neutral beam comprised primarily of CF_3 is generated and, as such, becomes the main etching species for Si_3N_4,during the patterning process. Additionally, surface polymerization and surface oxidation on SiO_2 and poly-Si can be precisely controlled by addition of O_2 and H_2 gases, respectively. As a result, moderately high selectivity of Si_3N_4 to both of Si (6.2:1) and SiO_2 (18.6:1) could be achieved by optimizing the ratio of $CF_3I/O_2/H_2$. Additionally, on relaxed ground rule structures at ~ 240nm pitch and gate CD (L_{gate}) ~ 40nm, an optimized NB etching condition achieves complete removal of the spacer from the gate sidewall with negligible spacer loss at the top of the gate structure and < 2 nm SOI loss. These results demonstrate the potential of silicon nitride etching process using neutral beams for fabricating sub-22-nm gate sidewall spacers.

10:40am **PS-MoM8 Highly Selective Etching of Titanium Nitride Over Tantalum Nitride in Inductively Coupled Plasma**, ***W. Zhu***, *H. Shin, S. Sridhar, L. Liu, V.M. Donnelly, D.J. Economou,* University of Houston, *C. Lenox, T. Lii*, Texas Instruments

The etching properties of metal nitrides (TiN, TaN) for high-k metal-gate integration were investigated in a Faraday-shielded inductively coupled plasma. The effect of operating conditions such as pressure, bias, and gas composition in HCl/He plasmas were explored for isotropic, highly selective etching of TiN over TaN. High selectivity is required for advanced device architectures incorporating metal gates integrated with high-k gate dielectrics and etch-stop layers. Etch rates were obtained separately for TiN and TaN blanket films on Si using end-point detection (by monitoring the Si 288nm emission signal) and reflectance measurements using a He-Ne laser, verified by post-etching TEM cross-sectional profiles. The etching rates were measured to be 130±20 and 60±10 nm/min for TiN and TaN, respectively, using 30% HCl/He chemistry at 70mTorr and 400W in continuous wave plasma with no bias on the substrate. The higher etching rate of TiN compared to that of TaN can be attributed to the lower binding energy of TiN and higher volatility of $TiCl_4$ etch byproducts. The etching selectivity was 2:1 (TiN:TaN) under the condition investigated. Higher selectivity between TiN and TaN was achieved by adding trace amounts of O_2 (O_2 partial pressure $<1x10^{-4}$Torr): for very small oxygen additions, the etching rate of TiN remained unchanged, whereas that of TaN decreased significantly. At high enough additions of O_2, etching of both TiN and TaN was completely suppressed. A narrow window of selectivity was found by varying O_2 partial pressure. The film surface was characterized after etching using X-ray photoelectron spectroscopy (XPS). Cl_2/He plasmas were also studied and their similarities and differences with HCl/He plasmas will be discussed.

Work supported by Texas Instruments.

11:20am **PS-MoM10 Detailed Analysis of Si Substrate Damage Induced by HBr/O_2- and H_2-Plasma Etching and the Recovery Process Designs**, *Y. Nakakubo, A. Matsuda,* Kyoto University, Japan*, M. Fukasawa,* Sony Corporation, Japan*, Y. Takao,* Kyoto University, Japan*, T. Tatsumi,* Sony Corporation, Japan*, **K. Eriguchi**, K. Ono*, Kyoto University, Japan

Hydrogen-containing plasmas have been widely used for fabricating Si-based electronic devices such as metal–oxide–semiconductor field-effect transistor (MOSFET). Plasma-induced Si substrate damage during shallow trench isolation and gate electrode formation processes has become one of the critical issues because the damaged structure is believed to not only degrade the electric performance but also enhance the parameter variations resulting in yield loss in mass production [1]. Due to its light mass, a hydrogen atom from plasma can penetrate deeper in Si substrate, and, consequently, forms the thicker damaged layer leading to the larger amount of Si loss in the source /drain extension region of MOSFET called "Si recess" [2]. Although the recovery mechanism of Si damage has been extensively studied, there have been few comprehensive process-design guidelines by taking into account the electrical characteristic degradation. In this study, we report detailed analyses of Si-damage recovery dynamics using a capacitance–voltage (C–V) technique, and provide respective recovery process guidelines for HBr/O2- and H2-plasma cases. Silicon wafers with thermal-oxide layer (2 nm) were damaged by HBr/O2-and H2-plasma treatments. Various annealing processes in N2 ambient with different "thermal budgets" were employed to address the impacts of the temperature and budget on the damage recovery. An SiO2-Capping layer was formed on some samples to simulate structural constraints in present-day MOSFET processes. Using the quantitative C–V technique (1/C2-based analysis), we found that, although HBr/O2-plasma induced a larger amount of Si damage (defect site), wet-etch stripping process was more effective due to thinner damaged layer thickness, further, the annealing process with temperatures higher than 850 ºC was found to be able to cure the structural defects. As for H2-plasma cases, on the other, the wet-etch was "insufficient" to remove the defects, resulting in a high conductive layer. Moreover, we observed that the annealing temperature (> 1050 ºC) rather than the budget was a primal parameter to cure the damage. The obtained results may be explained by "the defect-density or structural-constraint effect". The present findings imply an important and useful guideline of the recovery process design of H-containing-plasma damage in future advanced devices. [1] K. Eriguchi *et al.*: J. Vac. Sci. Technol. **A 29**, 041303 (2011).[2] M. Fukasawa *et al.*: J. Vac. Sci. Technol. **A 29**, 041301 (2011).

11:40am **PS-MoM11 Time-modulated Plasma Etching for Next Generation Devices**, ***S. Sriraman***, *Y. Wu, G. Kamarthy, C. Rusu, J. Holland, A. Paterson, V. Vahedi*, Lam Research

Plasma etching has facilitated the continuation of Moore's Law from >1µm to now less than 20 nm and is used to enable next-generation semiconductor device technology. While etching is used to compensate for incoming lithographic limitations as well as non-uniformities from up-stream processes, it also offers ways to counter fundamental limitations of pattern dependent etching and atomic-scale mixing. In this context, time-modulated plasma etching is the key to address challenges arising in critical etch applications for <20nm technology nodes.

This paper will aim to discuss some fundamental factors in consideration for time-modulated plasma etching in a Transformer Coupled Plasma (TCP™) chamber and its outcomes on representative process applications. Using a combination of experimental results, diagnostics, and modeling & simulation, the advantages of different types of time-modulated plasma and their ability to control basic plasma properties will be covered. The role and benefits of independently controlling ions and neutrals to overcome limitations in etching and their applicability to next generation device architectures will be discussed.

Plasma Science and Technology
Room: 24 - Session PS+BI-MoA

Applications of (Multiphase) Atmospheric Plasmas (including Medicine and Biological Applications)
Moderator: G.Y. Yeom, Sungkyunkwan University, Korea

2:00pm **PS+BI-MoA1 Plasmas in Saline Solution Sustained Using Bipolar Pulsed Power Source – Tailoring the Discharge Behavior Using the Negative Pulses**, ***H.W. Chang****, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Plasmas in saline solutions have been extensively studied due to their wide applications. In this work, plasmas ignited in saline solution were studied. The plasma system consisted of two electrodes immersed in 0.2 M NaCl saline solution. The electrode where the plasma was ignited was a 0.5 mm - diameter Pt wire covered by a glass tube to precisely define the area exposes to the solution. The grounding electrode was a bare platinum wire with the same diameter. Diagnostic tools used included voltage and current probes, an optical emission spectrometer, and a photomultiplier tube. We studied plasmas driven by a bipolar pulse power source using repetitive positive and negative voltage pulses with adjustable width and amplitude. We used the positive voltage pulses to ignite the plasma while using the negative voltage pulses to tailor the electrolytic gas formation amount. Conditions with the positive voltage pulse fixed at +600 V with an 80 μs duration, and the negative pulse varying from 0 to 80 V with the duration ranging from 0 to 20 ms were tested. By changing the duration of each voltage pulses, the bubble dynamics and the plasma behavior can be effectively controlled. By increasing the negative voltage pulse amplitude, we observed a decrease in the maximum currents before the ignition of the plasma from 1.75 to 1.0 A . The time required for plasma ignition upon the onset of the positive voltage pulse was reduced. The above observations can be well explained by the coverage of the electrode surface by electrolytic gas. Optical emission spectroscopy showed that I_H(656 nm)/I_{Na}(588 nm) ratio increases from zero to 0.0035 when the negative voltage pulse amplitude increases from 0 to 80 V. This clearly showed hydrogen, the electrolytic gas, content in the bubble increased with the increase in negative voltage pulse amplitude. This work was supported by National Science Council of Taiwan, the Republic of China (100-2628-E-002-012 and 101-3113-E-002-002).

2:20pm **PS+BI-MoA2 Low Temperature Plasma Deactivation of Endotoxic Biomolecules: The Effects on Lipid A**, ***T.-Y. Chung***, *J.-W. Chu, D.B. Graves*, University of California Berkeley, *E. Bartis, J. Seog, G.S. Oehrlein*, University of Maryland

Effective removal of infectious organisms and/or biomolecules from medical instruments is essential to prevent infections and disease transmission. Intricate modern instruments are difficult to clean via thermal sterilization since they are often heat sensitive. Furthermore, bacterial endotoxin and prion proteins are known to be particularly resistant to conventional sterilization procedures.[1, 2] Low-temperature plasma is a promising option for surface sterilization of bacteria and deactivation of harmful biomolecules, but mechanisms of endotoxic biomolecule deactivation are poorly understood.[3] Using a vacuum beam system, we study the effects of vacuum ultraviolet (VUV) radiation, oxygen and deuterium radicals on lipid A, the immune-stimulating region of lipopolysaccharide (LPS). The endotoxic activity of lipid A samples is monitored by measuring the secreted interleukin-1β (IL-1β) in human whole blood. The results obtained from *ex situ* transmission Fourier transform infrared (FTIR) spectroscopy, *in situ* quartz crystal microbalance (QCM), *in situ* residual gas analysis and *ex situ* electrospray ionization mass spectrometry (ESI-MS) show that VUV photons cause bulk modification to the penetration depth of photons, ~200 nm. On the other hand, radicals mainly cause chemical etching and modification near the surface of lipid A films. Although the radical-induced etch yield of lipid A is much lower than VUV-induced photolysis, secondary ion mass spectrometry (SIMS) and human whole blood-based assay demonstrate that O and D radicals alter the film surface, leading to significant reduction of film endotoxicity. Important structures governing the endotoxic activity of lipid A, e.g. the fatty acid chains and the phosphate groups, are greatly reduced after radical exposure. Qualitatively similar results are observed when LPS films are exposed to either H atoms or VUV photons in low-pressure plasma. The deactivation effects of low energy ions and atmospheric pressure air plasma on lipid A films will also be presented.

[1] K. L. Williams, ed., Endotoxins: Pyrogens, LAL Testing and Depyrogenation, Informa Healthcare USA, Inc., New York, 2007.

[2] W. A. Rutala and D. J. Weber, Infect. Control Hosp. Epidemiol. **31**, 107 (2010)

[3] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

2:40pm **PS+BI-MoA3 Nonthermal Bioplasma Sources and its Interactions to the Microbial, Fungal, Yeast and Living Cells**, ***E.H. Choi***, *Y. Kim, G.S. Cho, G. Kwon, B.K. Min, H. Uhm,* Kwangwoon University, Republic of Korea, *P. Suanpoot,* Maejo University Phrae Campus, Thailand, *G. Lee, R. Jung, B. Park*, Kwangwoon University, Republic of Korea **INVITED**

We have investigated the atmospheric pressure (AP) nonthermal bioplasma sources and their characteristics as well as their interactions with biological cells of microbial, fungal, yeast, and living cells. The electron temperature and plasma density are measured to be about 1.1 eV~ 1.5 eV and $(1{\sim}3)\times10^{12}$ cm^{-3} , respectively,for the direct plasma jet and dielectric barrier discharge (DBD) plasma under Ar gas flow. The densities for the reactive oxygen species (ROS) such as the hydroxyl radicals (OH), superoxide anions($O2^{*-}$), and nitric oxide (NO) have also been investigated in these AP direct plasma, respectively, inside the saline culture media by the ultraviolet optical absorption spectroscopy. Herein, we have investigated the basic interactions of these AP nonthermal bioplasma with the living organisms in morphological and biomolecular aspects. We found that the secondary electron emision coefficient of the biological surface has been drastically increased by atmospheric bioplasma, which indicates the biological surface to be oxidized especially by the hydroxyl (OH) radical species. In order to elucidate the basic mechanisms for the cell shrinking and apoptosis leading to a cell death by the nonthermal bioplasma, the cell membrane potential changes have been measured and investigated inside the culture media based on the ROS density as well as cell capacitances. It is also found that the molecular electron energy band structure in these biological cells have been modified and shifted toward the vacuum surface energy level by the AP nonthermal bioplasmas due to cell oxidation, mainly caused by OH radicals. We have also investigated the confocal Raman spectroscopy and circular dichroism as well as various biological assays to clarify these characteristics.

3:40pm **PS+BI-MoA6 Deactivation of Lipopolysaccharide and Lipid A by Radicals Produced in Inductively Coupled Plasmas**, ***E. Bartis***, University of Maryland, *T.-Y. Chung, J.-W. Chu, D.B. Graves,* University of California Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland

Low temperature plasma (LTP) treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules [1]. However, a major knowledge gap exists regarding which plasma species e.g. ions, VUV photons, and reactive radicals, are responsible for the modifications required for deactivation. Lipopolysaccharide (LPS) and lipid A, the toxic element of LPS, are the main components of the outer membrane of Gram-negative bacteria and are notoriously difficult to remove from surfaces by traditional sterilization methods [2]. In this study, LPS- and lipid A-coated silicon substrates were exposed to low pressure plasma-generated Ar and H radicals isolated from an inductively coupled LTP source by employing a gap structure [3] to examine the effects of plasma composition on etch rates and chemical properties. Bioactivity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA). Ar neutrals caused a 5% reduction in bioactivity whereas exposure to H radicals using the same plasma operating conditions caused a 25% reduction in bioactivity. Ellipsometric data shows that H radical-only exposures cause less than 2 nm of material removal, indicating that surface modification is the major cause of deactivation and that complete etching and removal is not necessary. These modifications can inhibit the binding of receptor molecules, whose binding depends on a variety of interactions such as hydrophobic and electrostatic interactions and lock-and-key mechanisms. After plasma processing, samples were characterized by vacuum transfer to x-ray photoelectron spectroscopy (XPS) to study the chemical changes occurring on the film surface. With XPS, we observed that plasma-generated H radicals produce a C-rich surface by effectively removing O, N, and P, the latter of which is from phosphate groups that contribute to the pyrogenicity. The C 1s spectra shows a clear loss of N-C=O and O-C=O groups. This loss leads to the removal of lipid A's aliphatic chains, which are responsible for its toxicity. Direct H2plasma treatments also remove O, but fast material removal causes an increase in N and P due to the exposed core and O-chain on LPS. Radical-only ELISA results will be compared to direct and VUV-only treatments where material removal is significantly

* Coburn & Winters Student Award Finalist

greater. This result is especially true for direct Ar plasmas, where modification/etching is dominated by ion bombardment. Our results compare favorably with complementary VUV/radical beam studies of lipid A.

[1] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

[2] E. T. Rietschel et al., FASEB J. **8**, 217 (1994)

[3] L. Zheng et al., J. Vac. Sci. Technol. A **23**, 634 (2010)

4:00pm **PS+BI-MoA7 Localised, Non-Contact Surface Modification with Microplasma for Biotechnological Applications**, ***S.A. Al-Bataineh***, *E.J. Szili, D.A. Steele, N.H. Voelcker, H.J. Griesser, R.D. Short*, University of South Australia

Localised surface modification of "open" surfaces is important for many biotechnological applications. In this study, we describe the utilisation of microcavity plasma arrays for localised surface modification of materials in a non-contact approach. In contrast to the current methods for localised surface modification, our method achieves spatially controlled surface modification without the use of a physical mask, photolithography or contacting the surface. Therefore, it provides the opportunity to reduce the number of modification steps and thus the cost of surface engineering processes. To this end, a 7 x 7 microcavity plasma array device (each cavity is separated by 500 µm and has a diameter of 250 µm with a depth of 55 nm) was manufactured and operated in helium at atmospheric pressure to generate, under optimised operating parameters, spatially separated modified regions on passivated surface coatings. The microplasma-patterned coatings were then used to control the spatial distribution of biomolecules such as proteins by allowing protein adsorption onto the modified regions whereas the rest of the coating remains non-fouling. Therefore, this approach resulted in spatially separated areas of immobilised protein. These surfaces were also used to control the spatial distribution of other biomolecules as well as living cells.

4:20pm **PS+BI-MoA8 Biocompatible Nanocomposites Synthesized by Gas-Liquid Phases Plasmas**, ***T. Kaneko***, *Q. Chen, R. Hatakeyama*, Tohoku University, Japan **INVITED**

Recently, multiphase plasmas, particularly gas-liquid phases plasmas have attracted much attention as fundamental and application researches [1], because the non-equilibrium plasmas in gas phase can produce the various kinds of chemically active ions and radicals which react with nano- and bio-materials stably existing in liquid. As one of the promising applications of the gas-liquid interfacial discharge plasmas (GLIDPs), the synthesis of various kinds of nanoparticles [2] is advantageous in that toxic reducing agents are unnecessary and the synthesis is continuous during the plasma irradiation. In addition, the GLIDPs are also used in the biomedical field, for example, the synthesis of gold nanoparticles (AuNPs) conjugated with biomolecules such as DNA. The DNA conjugated AuNPs (DNA-AuNPs) work as vectors to deliver DNA into living cells because the AuNPs can be efficiently manipulated by a light field. Furthermore, the DNA-AuNPs are attempted to be encapsulated into carbon nanotubes (CNTs) to protect the DNA from the ambient environment.

The GLIDP is generated between the bottom liquid and top metal electrodes in Ar gas (20 kPa) by applying a pulse voltage (20 kHz) to the liquid electrode. The liquid electrode consists of aqueous chloroauric acid trihydrate ($HAuCl_4$•$3H_2O$) (0.1 mg/ml) with DNA. A single-stranded DNA is used as the conjugated material, which consists of 30 bases of cytosine or guanine. In the synthesis of the DNA-AuNP encapsulated CNTs, double-walled carbon nanotubes (DWNTs) are adopted to be used because of their large inner diameter.

Depending on the DNA concentration, the resultant water-soluble AuNPs take on pink and purple. The different colors originate from the particle size and interparticle distance which determine the absorption wavelength of the surface plasmon resonance of the AuNPs. Interestingly, these phenomena depend on the types of DNA base, which are attributed to the difference in the binding energy of the DNA base. Therefore, we can control the size and assembly of the AuNPs by changing the DNA type and concentration [3].

In order to encapsulate the negatively charged DNA-AuNPs into the DWNTs, a positive DC voltage is applied to the DWNTs put on the substrate immersed in the GLIDP. The transmission electron microscope images of the resultant products show that the number of the DNA-AuNPs encapsulated into DWNTs increases with an increase in the positive DC voltage.

[1] T. Kaneko, K. Baba and R. Hatakeyama: J. Appl. Phys. **105**, 103306 (2009).

[2] T. Kaneko, Q. Chen, T. Harada and R. Hatakeyama: Plasma Sources Sci. Technol. **20**, 034014 (2011).

[3] Q. Chen, T. Kaneko, and R. Hatakeyama: Chem. Phys. Lett. **521**, 113 (2012).

5:00pm **PS+BI-MoA10 Organization of Dielectric Barrier Discharges in the Presence of Structurally-Inhomogeneous Wood Substrates**, *O. Levasseur,* Université de Montréal, Canada, ***A. Bouarouri****, N. Naudé, R. Clergereaux, N. Gherardi,* Université de Toulouse, UPS, INPT, LAPLACE, France, *L. Stafford*, Université de Montréal, Canada

There has been a growing interest in the use of dielectric barrier discharges (DBDs) for many applications, especially for the treatment of heat-sensitive materials such as polymers. Some studies have also reported a self-organization of these discharges which can manifest itself in two ways : i) the auto-organization of filaments or micro discharges in a filamentary DBD or ii) the formation of regular spatio-temporal patterns in a glow-like discharge. Several types of patterns such as hexagonal arrays or concentric rings have been observed for various gases and system configurations. We have recently extended the range of applications of DBDs to the functionalization of wood surfaces with the objective of improving its durability following natural weathering. However, the application of DBDs to the modification of wood presents additional complications compared to traditional substrates due not only to the highly porous nature of wood which can produce significant outgassing but also to the presence of "early" vs. "late wood" sections which can introduce local modification of the properties of the dielectric exposed to plasma. In this work, we examine the organization of DBD in the presence of complex wood substrates using optical imaging and current-voltage (I-V) characteristics. For Douglas pine samples, the structural inhomogeneities of the wood substrate was found to produce non-uniform light emission patterns while maintaining homogeneous-like I-V characteristics. Experiments performed on samples with various fractions of "early" vs. "late" wood sections showed that the plasma emission was always more intense on the "early" wood. The charge flow pattern was also analyzed using surface potential measurements. Both sections exhibited decaying behaviors, with time constants, t, of 40 s for late wood and 10 s for early wood. Based on these results and the predictions of a simple electrical model of the discharge, the organization was ascribed to a spatial modulation of the relative dielectric permittivity on "early" versus "late" wood affecting the local voltage applied to the gas, and thus the local discharge current which is directly related to the plasma emission.

5:20pm **PS+BI-MoA11 Role of Substrate Outgassing on the Formation Dynamics of Either Hydrophilic of Hydrophobic Wood Surfaces in Atmospheric-Pressure, Organosilicon Plasmas**, ***O. Levasseur****, L. Stafford,* Université de Montreal, Canada, *N. Gherardi, N. Naudé,* Université de Toulouse, UPS, INPT, LAPLACE, France, *P. Blanchet,* FPInnovations, Canada, *B. Riedl,* Université Laval, Canada, *A. Sarkissan*, Plasmionique, Canada

Dielectric barrier discharges (DBDs) were thoroughly investigated over the last several years with one of the main goals being the achievement of a homogeneous discharge at high operating pressure in various gas mixtures. This keen interest is mainly driven by the fact that atmospheric-pressure DBDs present major advantages over low-pressure plasmas for polymer treatments, one of the most important being the ability to work with cold plasmas without the use of high-end vacuum pumping systems. Over the last decade many precursors, such as organosilicon compounds like hexamethyldisilazane (HMDSN) and hexamethyldisiloxane (HMDSO), were added to these cold, atmospheric-pressure plasmas for PECVD applications and a wide variety of coatings have been obtained by such methods. Application of DBDs to the treatment of polymers is however much more challenging than for conventional substrates such as Si or SiO2. This can be not only be attributed to the highly complex chemical nature of most polymers but also to their generally porous microstructure which can release impurities in the discharge either from plasma-substrate chemical reactions or from sample outgassing (if not pumped-down beforehand). Such impurities can greatly alter the discharge stability and gas-phase kinetics which are both known to play an important role on the plasma deposition dynamics. In this work, we capitalize on the very porous nature of wood to examine the influence of substrate outgassing during PECVD on the stability of a N_2-HMDSO discharge and on the evolution of the properties of plasma-deposited thin films over sugar maple and black spruce wood samples. Current-voltage characteristics revealed a transition from a filamentary to a homogeneous discharge with increasing plasma treatment time, t. Based on optical emission spectroscopy, the filamentary behavior was ascribed to the release of air and humidity from the wood substrate following plasma exposure which produced significant quenching of N_2 metastables. This effect vanished at longer treatments times due to the nearly complete "pumping" of products from the substrate and the progressive deposition of a "barrier" layer. Analysis of the surface wettability through static, water contact angles (WCAs) and of the surface composition through FTIR and XPS indicated that for $t < 10$ min, the wood surface was more hydrophilic due to the formation of a SiO_x layer, a typical

behavior for HMDSO deposition in presence of oxygen. On the other hand, for $t > 10$ min, the static WCA increased from ~50º up to ~140º due to the deposition of hydrophobic $Si(CH_3)_3$-O-$Si(CH_3)_2$ and $Si(CH_3)_{3,2}$ functional groups.

Plasma Science and Technology
Room: 25 - Session PS2-MoA

Plasma Modeling
Moderator: E. Despiau-Pujo, LTM-CNRS

2:00pm **PS2-MoA1 Tailored Ion Energy Distributions on Plasma Electrodes**, ***P. Diomede***, *D.J. Economou, V.M. Donnelly*, University of Houston **INVITED**

Control of the energy of ions bombarding a substrate is important for both plasma etching and deposition. As device dimensions keep shrinking, requirements on selectivity and substrate damage become ever more stringent. Such requirements impose strict limits not only on the mean ion energy but also of the ion energy distribution (IED). The IED may be controlled by applying judicious bias voltage waveforms on the substrate, or on a "boundary electrode" in contact with the plasma. A Particle in Cell simulation with Monte Carlo Collisions (PIC-MCC) was employed to predict the IEDs resulting by the application of a variety of voltage waveforms (steps, staircases , etc.) on a plasma electrode in the afterglow of power-modulated plasmas. IEDs with distinct energy peaks at controlled location, spacing, and fraction of ions under each peak, were obtained by properly selecting the applied waveform. The effect of gas pressure on the IEDs was also studied. A semi-analytical equivalent-circuit model was developed to solve the "inverse problem", i.e., to find the voltage waveform that results in a desired IED. The model allowed rapid calculation of the IED, and model predictions were in agreement with experimental data and the results of the much more computationally intensive PIC simulation. Work supported by DoE Plasma Science Center and NSF.

2:40pm **PS2-MoA3 Self-Consistent Multi-Dimensional Modeling of Inductively Coupled Plasmas**, ***A. Agarwal***, *J. Kenney, M.-F. Wu, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma etching of microelectronic structures at advanced technological nodes (< 2x nm), especially complicated structures such as multi-gate MOSFETs and 3D memory stacks, places great emphasis on uniformity of the process.[1] Asymmetries, either azimuthal or radial, can arise in inductively coupled plasma (ICP) sources due to the input and pumping locations of feedstock gases, voltage and current variations along the coils, and other particulars of the reactor configuration.[2] While two-dimensional plasma models are adequate to tackle radial non-uniformities during design of ICP systems, these models usually do not address the circuit issues and are incapable of investigating azimuthal asymmetries.

In this work, results from a two-dimensional plasma model, HPEM[3], modified to include match-side circuit calculations, will first be discussed to highlight the effect of coil voltages on capacitive coupling in ICPs. The model is validated using voltage and current measurements in the match and along the coils. The consequences of capacitive coupling on the plasma and ion energy distribution characteristics will be discussed.

With increasing coil dimensions, voltage and current can vary along the coils which can produce azimuthal asymmetries. Mitigation of these non-uniformities requires a careful antenna design. However, as these azimuthal non-uniformities cannot be predicted by a two-dimensional model, a three-dimensional model is required to help with antenna design for ICPs. We discuss results from three-dimensional modeling of ICPs using the plasma-electromagnetics modeling code, Mira.[4] Mira is a fully electromagnetic fluid plasma model which self-consistently computes the electromagnetic fields using the finite-difference time domain (FDTD) technique. By virtue of the fully electromagnetic nature of the model, both capacitive and inductive fields are self-consistently included while computing the power deposition in the plasma. The effect of various azimuthally asymmetric reactor configurations and coil designs on plasma uniformity will be discussed.

[1] K. Ahmed and K. Scheugraf, IEEE Spectrum 48 (11), 50 (2011).

[2] J.A. Kenney, S. Rauf, and K. Collins, J. Appl. Phys. 106, 103302 (2009).

[3] M.J. Kushner, J. Phys. D 42, 194013 (2009).

[4] S. Rauf, Z. Chen, and K. Collins, J. Appl. Phys. 107, 093302 (2010).

3:00pm **PS2-MoA4 Feature Profile Modeling of STT-MRAM Etch**, ***P. Stout***, Applied Materials Inc.

Results of feature profile evolution modeling of a STT-MRAM (Spin Transfer Torque - Magnetoresistive Random Access Memory) etch process will be discussed. STT-MRAM is a promising candidate for future memory. This non-volatile RAM has fast read/write, is scalable to DRAM (dynamic random access memory) cell sizes, has low power, and has possible multi-bit multi-level capability. This talk will address modeling the pattern definition of the MTJ (magnetic tunneling junction) stack through an etch process. The feature model used for the study is a 3D Monte Carlo model. The MTJ stack consists of many metals which are not easily etched (i.e., mostly non-volatile etch by-products) such as CoPt, Ru, CoFeB, and MgO. Thus, the feature model assumes mostly physical sputtering as the etch mechanism. The material emission model is also important in a physically dominated etch process. The impact of different material emission models on the final profile will be discussed. The main issue is removal of metal sidewall deposits which are the result of the re-deposition of the sputtered MTJ layers. The thickness of the re-deposited metal on the sidewall decreases from bottom to top. The closer the sidewall is to the sputter source at the feature bottom the thicker the deposit. The thickness is also heavily influenced by the geometry of the mask. Given the physical nature of the etch line-of-sight of incoming ions and outgoing metal is important. Negative sidewall slopes can also influence the morphology of the re-deposited metal. The square shaped pillar patterns modeled have non-uniform deposit around the circumference of the feature with larger metal at the corners. The etch front is also more non-uniform due to the length difference from corner to corner vs side to side for the features. Smaller aspect ratio features will allow removal of more MTJ metal but may have less of an impact on the final CDat the MgO layer. Material sputter emission models which are more focused lead to thicker deposits in sputtered layers, spottier deposits on patterned sidewalls, and ledge formation. The difficulty in removing the metal sidewall deposits leads to strategies such as the use of off-angle ion beams. Off-angle ion beams take advantage of the off-angle peaks in the ion yield curves. The number of steps per rotation and the off-angle value influence the final profile. Fewer steps / rotation lead to more non-uniform etch fronts. Larger off-angles lead to larger yield numbers for the sidewall deposited metal but will also be shadowed by nearby features limiting the depth where the metal removal takes place.

3:40pm **PS2-MoA6 Development of a New Industry Focused Plasma Simulation Tool**, ***A.I. Williams***, University College London, UK, *S. Lopez-Lopez,* Quantemol Ltd., UK, *W. Brigg, J. Tennyson*, University College London, UK

Plasma processes are routinely used in a number of industrial settings, for applications varying from silicon chip etching to thin-film deposition for solar cells. In the majority of these cases the techniques and procedures used to create the required plasmas are obtained by initial experimental trial and error. Thus, this advancement has been led in a large part by the technical ability of the engineers in charge of the equipment. This model has worked so far, however, with more and more complex plasma chemistries being developed and the continual drive for efficiency, simulations are becoming another implement in the engineer's toolset. This poses interesting requirements on any simulation software which is aimed toward industry, such as: reliability, simulation speed and ease of set-up. It is the goal of the new coding project at UCL and Quantemol Ltd. to tackle these issues and more, to produce a simulation tool specifically targeted to industrial applications.

This new software will allow the simulation of full 3D geometries, implementing a finite element method (FEM) to solve the required partial differential equations and a hybrid simulation method to improve runtime. We intend to implement the following features:

An underlying robust FEM library, which includes automated mesh refinement.

Parallel computation of the FEM to decrease runtime.

Simplification of plasma chemistry creation with a look at automatic generation through linking with pre-built databases.

Automated selection of plasma models through algorithmic selection to help speed up the set-up and improve the quality of simulations.

A robust test suite of simulations to assure validity of results.

At the conference the latest research issues about, and the development towards the above features will be reported.

4:00pm **PS2-MoA7 Mechanism of Generating Ions and Radicals in Fluorocarbon Plasma Investigated by Reaction Model Analysis**, ***Y. Kondo****, *Y. Miyawaki, K. Takeda, H. Kondo, K. Ishikawa, T. Hayashi, M. Sekine, M. Hori*, Nagoya University, Japan

Excellent etch properties such as high etch rate, high selectivity, fine profile, are required for interlayer dielectric film processing for ULSI circuits to achieve high device performances. The etch properties depend on the composition and amount of active species, i.e. ions and radicals which are strongly correlated with the molecular structure of feedstock gas. To choose the most appropriate feedstock gas for designing a specific etch process, it is favorable to understand the detailed relationship among gas molecule structure, active species and etch performance. It may also lead to suggest a new gas with extreme high performance.

In previous study, we have developed a SiO_2 etch process using CF_3OCFCF_2 (C_3F_6O). C_3F_6O has characteristic molecular structures such as an ether bond, a CF_3 group and a double bond. Relatively high etch rate for SiO_2 is expected for the C_3F_6O plasma chemistry since the major fragment ion of C_3F_6O is CF_3^+ that is known to show high etch yield for SiO_2[1]. Detailed relationship among the gas molecule structure, etch species and etch performance, however, has not clarified so far.

In this study, we have developed a chemical model of reactions in C_3F_6O/Ar plasma and simulated it using chemical kinetics simulation software, CHEMKIN. The experimental results were compared with the results obtained by the model. Then, we clarified the generation pathway of ions and radicals, and evaluated effects of the difference of these pathways on the composition of active species. Then we considered the relationship between molecule structure and the generation of active species.

Electron induced dissociation channels of C_3F_6O were evaluated by analysis of cracking patterns measured using a quadruple mass spectrometer. Cross-section for ionizing dissociation of C_3F_6O was estimated through a range between a few to 50 eV for electron energy [2]. Reaction constants for this dissociative ionization were calculated by integrating over whole electron energy range assuming the electron temperature as 3 eV. Using these constants and constants on previous model for CF_4, C_2F_6, and C_4F_8 chemistry [3, 4], the chemical model of gas phase reactions in the C_3F_6O/Ar plasma was constructed, and enabled us to estimate the concentrations for gas phase species. We also evaluated the dependence of the concentrations on electron density, partial pressure of feedstock C_3F_6O gas and residence time.

[1] K. Karahashi, et al. : J. Vac. Sci. Technol. A **22**, 1166 (2004).

[2] H. Toyoda, et al. : Jpn. J. Appl. Phys. **36**, 3730 (1997).

[3] G. I. Font et al., J. Appl. Phys. **91** (2001) 6.

[4] A. V. Vasenkov et al., J. Vac. Sci. Technol. A **22** (2004) 3.

4:40pm **PS2-MoA9 Excitation of Ion Acoustic Waves by Electron Beams**, *I.D. Kaganovich,* Princeton Plasma Physics Laboratory, ***D. Sydorenko***, University of Alberta, Canada, *E. Tokluoglu, E.A. Startsev, A.V. Khrabrov,* Princeton Plasma Physics Laboratory, *L. Chen, P. Ventzek, R. Sundararajan*, Tokyo Electron America

The interaction of an electron beam with plasma is of particular importance for hybrid DC/RF coupled plasma sources used in plasma processing. A high frequency (HF) electron plasma wave resonant with the high-energy beam may decay into another HF wave and an ion acoustic wave. The new HF wave may have lower phase speed than the original HF wave. Electron acceleration by the slower HF wave may explain the low-energy peak in the electron energy distribution function measured in plasma processing devices [1]. In the present paper, the collisionless electron heating in a hybrid RF-DC plasma source is studied using the particle-in-cell code EDIPIC. [2,3] In simulation, electrons emitted from the cathode surface are accelerated through a dc bias electric field and form an 800 eV electron beam entering the bulk plasma. The beam excites electron plasma waves through the two-stream instability. High localized plasmon pressure creates ion acoustic waves in the process similar to the modulation instability. Eventually, coupling between electron plasma waves and ion acoustic waves deteriorates HF oscillations, which leads to bursting behavior.

[1] L. Chen and M. Funk, Langmuir wave standing wave resonance in DC/RF plasma, Proceedings of ICRP 2010.

[2] D. Sydorenko, A. Smolyakov, I. Kaganovich, and Y. Raitses, Phys. Plasmas, **14,** 013508 (2007).

[3] D. Sydorenko, I. Kaganovich, Y. Raitses, A. Smolyakov, Phys Rev Lett., **103**, 145004 (2009).

5:00pm **PS2-MoA10 Multi-Peaked and Stepped Electron Velocity Distributions in RF-DC Discharges with Secondary Emission**, ***A.V. Khrabrov***, *I.D. Kaganovich,* Princeton Plasma Physics Laboratory, *D. Sydorenko,* University of Alberta, Canada, *E. Tokluoglu, E.A. Startsev,* Princeton Plasma Physics Laboratory, *L. Chen, P. Ventzek, R. Sundararajan*, Tokyo Electron America

In RF-DC (hybrid) capacitive-coupled discharges, secondary electrons emitted from the electrodes undergo a complicated motion defined by acceleration in, and bouncing between a steady and an oscillating sheath. For the electrons that return to the RF electrode, the arrival phase is a multi-valued function of the phase in which they were emitted. This basic property leads to a velocity distribution with multiple peaks. The phase of arrival can also be discontinuous, which corresponds to a distribution containing steps. We have observed such distributions in numerical test-particle simulations, and analyzed the observed structure of the electron distributions.

5:20pm **PS2-MoA11 Simulations of the Radial Line Slot Antenna Plasma Source**, ***P. Ventzek***, Tokyo Electron America, *S. Mahadevan,* Esgee Technologies, *J. Yoshikawa,* Tokyo Electron Technology Development Institute, INC., *L. Raja,* University of Texas at Austin, *T. Iwao,* Tokyo Electron Technology Development Institute, INC., *L. Chen, R. Sundararajan, J. Zhao,* Tokyo Electron America, *T. Nozawa, K. Ishibashi,* Tokyo Electron Technology Development Institute, INC., *R. Upadhyay*, Esgee Technologies

The Radial Line Slot Antenna plasma source couples microwave power through a slot antenna structure and window to a plasma characterized by a generation zone adjacent to the window and a diffusion zone that contacts a substrate. The diffusion zone is characterized by a very low electron temperature. This property renders the source useful for soft etch applications and thin film processing for which low ion energy is desirable. The coupling between the microwave applicator, slot antenna, coupling window and plasma is complex and the subject of many investigations more often than not electromagnetic wave analysis. Another way to look at the coupling is that of a microwave network ending in a plasma load. A systematic analysis of the interrelationship between slot geometry, position and basic coupling window characteristics is presented revealing the complex impedance relationship between critical elements. We will begin presenting results from 2 dimensional plasma simulations illustrating sensitivity of the coupling to slot location using a single slot then go on to more complex examples. The plasma load itself adds additional challenges. In particular the importance of the high frequency behavior of the electron energy distribution function on the plasma load will be presented. Ignoring the impact of the driving frequency on the electron energy distribution function leads to significant variation in plasma predicted densities.

* Coburn & Winters Student Award Finalist

Plasma Science and Technology
Room: 24 - Session PS1-TuM

Plasma Diagnostics, Sensors and Control 1
Moderator: V. Nagorny, Mattson Technology

8:00am **PS1-TuM1 Monitoring Plasma Etch Processes with Wave Cut-Off, Langmuir, and Radio-Frequency Probes**, ***M.A. Sobolewski***, National Institute of Standards and Technology (NIST) **INVITED**

In industrial plasma etching processes, etch rates, profiles, and the critical dimensions of etched features may depend very sensitively on ion current density and other plasma parameters. The reproducibility of plasma conditions is thus an important concern, but the many mechanisms that can cause plasma properties to vary during processing have not been much studied. Here, such mechanisms were investigated using a wave cut-off probe and a Langmuir probe, in tetrafluoromethane/argon plasmas in an rf-biased, inductively coupled plasma reactor. The wave cut-off probe provided measurements of plasma electron density every few seconds. Because it is based on a frequency measurement, it can precisely measure small changes in electron density, often as small as 1 %. Internal resonances in the cut-off probe, however, can degrade this precision. The Langmuir probe provided measurements of the ion current density, electron and ion densities, and electron energy distribution function, with a time resolution of tens of seconds.

Several different phenomena were investigated. First, we investigated the changes in plasma electron density that occur when the rf bias is turned on or off. Analysis shows that such changes can be explained by the stochastic heating of electrons by rf bias power, the interaction of the rf bias and the inductive source, and perturbations in gas composition caused by etch products. Second, we investigated the changes in all plasma parameters that occur when etches of silicon dioxide films on silicon substrates reach endpoint. Analysis shows that the changes observed at etch endpoint were primarily due to changes in gas composition, rather than changes in electron emission from the wafer surface. Third, we also observed nonidealities in the inductive source that affect its ability to maintain constant plasma parameters.

Simultaneous with these measurements, the rf current and voltage were measured outside the reactor, in the rf bias and inductive source circuitry. These external measurements were strongly correlated to — and explained by — the wave cut-off and Langmuir probe data. These results strongly suggest that nearly all of the phenomena observed here can be monitored equally well by external rf measurements, instead of invasive probes.

8:40am **PS1-TuM3 Impact of Self-Absorption on Emission Spectral Lines for Non-Equilibrium Plasma Source**, ***E. Gudimenko***, *V. Milosavljevic, S. Daniels*, Dublin City University, Ireland

Precise optical measuring techniques of spectral lines are necessary for low pressure plasma semiconductor manufacturing analysis. Problems which add to the inaccuracy of the optical measuring techniques include spectral line broadening mechanisms such as self-absorption.

Self-absorption has been widely neglected or its importance overlooked for plasma diagnostics.

In this study several different techniques are used to examine the impact of self-absorption on emission spectral lines from a reactive ion etch (RIE) plasma chamber, measured using a high resolution optical spectrometer. The experiments are performed in an Oxford Instruments plasma lab 100 RIE chamber which operates at a standard single frequency (GEC) 13.56 MHz with maximum RF power of 600 W. The OES spectrums were taken with a Horiba Jobin Yvon Czerny-Turner design Auto MicroHR spectrometer with focal length of 140 mm and spectral resolution of 0.25 nm at 400 nm wavelength.

One technique which is used is to check line intensity ratios within multiplets which abide by so-called LS-coupling rules. The time or spatial fluctuation in the observed intensity of the strongest or metastable line within the multiplet, in respect to the weakest spectral line in the same multiplet shows that self-absorption is present. Another technique which is examined is to change the optical path length by measuring the plasma from different points or different viewports on the plasma chamber. If the increase in signal intensity changes corresponding to optical path length, there is no self-absorption.

A Design of Experiments (DOE) has been used to cover the multidimensional external parameter space e.g. power, pressure, flow rate and chemistry. The results from the techniques are compared to each other for accuracy and the impact of self-absorption is then quantified. In this work the influence of self-absorption of neutral Argon and Oxygen spectral lines for a range of parameters in an RIE plasma chamber has been studied. Almost all the measured spectral lines have been affected, up to some level, by self-absorption. Some spectral lines shapes are changed by self-absorption up to 60%. One of the most widely used actinometry spectral lines for plasma diagnostics, Argon 750 nm, has its intensity affected by self-absorption by up to 40%.

Correction of self-absorption is a necessary step for OES based plasma diagnostics. In the case of Actinometry calculation correction of self-absorption could change the final result up to 20%.

This material is based upon works supported by Science Foundation Ireland under grant No.08/SRC/I1411

9:00am **PS1-TuM4 Real-Time Plasma Deposition Thickness Control using *In Situ* Optical Emission Interferometry**, *D.J. Johnson,* ***K.D. Mackenzie***, *C.W. Johnson, L. Martinez*, Plasma-Therm LLC

Measurement of the thickness of a growing film as it is deposited can provide real advantages in a production environment. Consistent film thickness is achieved despite long term process drifts and machine to machine variations in deposition rate. Also the time lost due to system re-qualification after routine cleans and maintenance procedures can be reduced significantly.

In this work film thickness is measured in situ in a PECVD system by reflectance techniques, using the plasma emission as a light source (Optical Emission Interferometry, OEI). A parallel plate deposition **system** is described in which the plasma emission reflected from the substrate is monitored through one of the gas introduction holes in the upper electrode. During the deposition of silicon dioxide and silicon nitride films, the emission bands from molecular nitrogen in the 300 – 400nm region are used for measurement purposes. As the film thickness increases the reflected intensity undergoes a cyclical variation due to interference effects. The film thickness change for one complete cycle is known from the values of the wavelength and the refractive index of the film at that wavelength. The number of interference cycles, including fractional cycles is counted and the film thickness calculated in real time as the film is deposited. The process is terminated when the desired film thickness is reached. An example is shown where the long term variation in film thickness is significantly reduced as compared to running a process terminated by time alone.

For thin films (eg < 100nm) a series of interference cycles is not generated, so the “peak counting” approach cannot be used. Instead, multiple wavelengths (multiple nitrogen bands) are monitored, generating more data points which permits a more accurate determination of the film thickness. This approach is applied to the deposition of a 50nm silicon nitride film.

The above approaches strictly measure change in film thickness, not absolute film thickness. It is shown that by monitoring the complete spectrum and calculating the spectrum change with time, the result is equivalent to the differential of the film's reflectance spectrum. From this the absolute film thickness is calculated. This is particularly useful for the deposition of thicker films where a final film thickness is required, despite a variable or unknown starting film thickness. Although not discussed here, the same approach can be used when etching thick films down to a final required thickness.

9:20am **PS1-TuM5 Subsequent Temporal Change of Gaseous H and N Radical Density in Plasma after Different Processes**, ***T. Suzuki***, *A. Malinowski, K. Takeda, H. Kondo, K. Ishikawa,* Nagoya University, Japan, *Y. Setsuhara,* Osaka University, Japan, *M. Shiratani,* Kyushu University, Japan, *M. Sekine, M. Hori*, Nagoya University, Japan

A precise shape control at less than 1 nm scale is demanded in large-scaled-integrated-circuits (LSI) fabrication of the 10-nm half pitch and beyond. In realization of super-fine plasma etching process, surface reactions of ions and radicals play important role because they determine etched feature [1]. Thus control of actual plasma parameters such as substrate temperature, radical density, and electron density is required. It has been proved that the radical density is changed as a result of emission into bulk plasma both of etching products and adsorbed species on chamber wall. However, investigation of influence of inner wall condition on bulk radical density has not been studied yet. Thus, in this study we focused on gaseous radical density in H_2/N_2 plasmas, and investigated temporal changes subsequently after different kind of plasmas where inner wall condition could be changed.

Measurements of gaseous radical densities have been carried out by the Vacuum Ultra Violet Absorption Spectroscopy (VUVAS) equipped with a micro-discharge hollow cathode lamp (MHCL) [2]. In this case we measured transition lines for Lyman α at 121.6 nm for H atoms and $^4P_{5/2}$-$^4S^0_{3/2}$, $^4P_{3/2}$-

$^4S^0_{3/2}$ and $^4P_{1/2}$-$^4S^0_{3/2}$ at 120.0 nm for N atoms. H_2/N_2 plasma was generated in a 100-MHz capacitively coupled plasma (CCP) reactor with H_2/N_2 gas mixture ratio of 75/25. Applied power was 400W (100 MHz) for upper electrode, and 200W (2 MHz) for bottom electrode respectively. The gaseous radical densities for the H_2/N_2 plasmas were monitored subsequently after different plasmas, (a) seasoning condition of H_2/N_2 plasma, (b) O_2 plasma, and (c) air exposure.

First, temporal changes for N radical density in the H_2/N_2 plasma subsequently, after the various plasma exposures were compared. In case of (a) seasoning, the N density was stable. On the other hand, the N radical densities were much varied after (b) O_2 plasma, and (c) air exposure. Notably, the density just after H_2/N_2 plasma ignition reached value which is more than twice higher when compared to stabilized value for (a) seasoning. Interpretation can be given as etched products or process gases were adsorbed on inner wall surface at the previous process, and then those species were desorbed from the wall into bulk plasmas in the subsequent processes. In accordance with organic *low-k* etching using H_2/N_2 plasmas, when a ratio of H radical and N radical (H/(H+N)) was changed more than 15% against an optimal original value, a shape of etched feature is resulted in modifications with scales of 10 nm [1].

[1] M. C. Sung *et al*, J. Appl. Phys. **107**, 113310 (2010).

[2] S. Takashima *et al*, J. Vac. Sci. Technol. A **19**, 599 (2001).

10:40am **PS1-TuM9 Experimental Implementation of Real-time Multivariable Control of a Capacitively Coupled Plasma**, ***Y. Zhang***, *B.J. Keville, C. Gaman, A. Holohan, M. Turner, S. Daniels*, Dublin City University, Ireland

The ever-increasing demand for higher device density in integrated-circuit fabrication has resulted in stringent requirements in respect of quality, reliability and precision of all fabrication processes in semiconductor manufacturing. *Reactive Ion Etching* (RIE) is a critical technology used at many stages of the manufacturing process. At present, most semiconductor manufacturing equipment is operated in open loop mode. Consequently, key plasma parameters such as ion flux and radical densities at the substrate surface are sensitive to drift in tool subsystems, changes in wall condition and wafer loading, for example. Such disturbances may affect process metrics such as etch depth and anisotropy and result in a significant degradation in device yield and performance.

In this presentation, we describe the implementation of a multi-variable *Linear Quadratic Gaussian/Loop Transfer Recovery* (LQG/LTR) controller to regulate key plasma parameters in an updated Mini-lab RIE 80 capacitively coupled chamber. The custom designed, real-time data-acquisition and control system has been implemented in Labview on a National Instrument CompactRIO real-time controller, which has been interfaced to a hairpin resonance probe and an optical emission spectrometer, the Ocean Optics USB4000. Experimental results are presented which compare the performance of the multivariable LQG/LTR controller to that of a suite of decentralised *single-input-single-output* (SISO) controllers.

This research forms part of program to implement multivariable closed-loop control on an industrial *Electron Cyclotron Resonance* (ECR) plasma etch chamber. The presentation concludes by describing progress in this part of the program.

11:00am **PS1-TuM10 Multivariable Control of a Capacitively Coupled Plasma**, ***B.J. Keville***, *Y. Zhang, M. Turner*, Dublin City University, Ireland

Present practice in reactive ion etching specifies etch recipes in terms of inputs such as gas flow rates, RF power and pressure. However, ostensibly identical chambers running identical recipes may produce very different results. Extensive 'chamber matching', i.e. initial iterative, empirical tuning of the process recipe, which entails time-consuming, ex situ statistical analysis of etch metrics, is required to ensure that an etch chamber produces acceptable results. Once matched, etchers are run 'open loop' and are thus sensitive to disturbances such as actuator drift, wall seasoning and substrate loading, which may have deleterious effects on process metrics such etch depth, uniformity, anisotropy and selectivity,. An alternative approach, which would reduce sensitivity to disturbances of the plasma generating process, would be to specify a recipe in terms of plasma quantities such as radical densities, and to regulate these in real time by adjusting the inputs with a suitable multivariable control algorithm.

Multivariable closed loop control of an $SF_6/O_2/Ar$ plasma in an Electron Cyclon Resonance (ECR) etcher is the focus of a major research program in the National Centre for Plasma Science and Technology (NCPST) in Dublin City University (DCU). As an intermediate step, a multivariable LQG/LTR control algorithm has been implemented on a capacitively coupled plasma using the same gas mixture. This presentation describes the design of the algorithm, and its efficacy is demonstrated via simulation with a variety of disturbances. The performance of the multivariable algorithm is compared to that of a suite of decentralised single-input-single-output (SISO) controllers.

11:20am **PS1-TuM11 Single and Multi-Point Ion Energy Distributions in a VHF+RF Commercial Reactor Measured by Novel In-Wafer Ion Energy Analyzer**, ***B.G. Lane***, *M. Funk, L. Chen, R. Sundararajan, J. Zhao*, Tokyo Electron America

The energy distribution of the ions impacting the wafer is a key determinant of process results. A novel, all silicon, minimally perturbing, non-contaminating, in-wafer, 2 and 3 layer ion energy analyzer described elsewhere in this conference is used to measure ion energy distributions for a variety of realistic processing conditions in a commercial VHF + 13.56 MHZ RF reactor with no modifications to its basic geometry or RF delivery system. Spectra with energies as high 1 keV are measured with resolution on the order of 1%. Total ion transmitted flux as well as the floating potential of the plasma exposed 1st grid relative to ground are measured in addition allowing estimates of the plasma potential at the sheath edge. Measured energy spectra are compared to particle simulations aiding in the interpretation of the spectral features. We show data and discuss the splitting of the high energy peaks due to finite ion sheath crossing time effects and how this splitting scales with frequency, power and pressure. We discuss how such splitting can be used to estimate the ion density at the sheath edge. We discuss the origin and scaling of charge exchange peaks. We use the identification of atomic and molecular oxygen ion peaks to estimate the resolution of the diagnostic . The use of VHF to obtain narrow ion energy distributions at moderate ion energies will be highlighted. Spectra using a multi-point, 2 layer variant of the ion energy analyzer design were obtained at 4 radial locations for a variety of conditions in argon and oxygen plasmas. These spectra quantify center to edge variations and reveal unique spectral features due to pre-existing modifications to the test reactor's upper counter electrode surface. We believe that these may be the first reported measurements of ion energy distribution functions for some of the more extreme conditions investigated and some of the first reported multi-point ion energy spectra for a commercial plasma reactor.

11:40am **PS1-TuM12 Characterizing Electron Beam Generated Plasmas for Plasma Processing Applications**, ***D.R. Boris***, *R. Fernsler, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas have a variety of unique features that make them distinctive plasma sources for materials processing. They are characterized by high plasma density, very low electron temperature, and unique gas phase chemistries that distinguish them discharge based plasmas. This work presents frequency probe and Langmuir probe measurements (where applicable) of plasma density over a range of 10^9 to 10^{12} cm^{-3} in a variety of processing plasma chemistries. This work also features the effect of varying gas chemistry on energy distribution function measurements as well as OES (optical emission spectroscopy) and mass spectrometry measurements.

Plasma Science and Technology
Room: 25 - Session PS2-TuM

Advanced FEOL/Gate Etching 2
Moderator: J.P. Chang, University of California at Los Angeles

8:00am **PS2-TuM1 Gate-Silicon Etching using Evanescent Microwave Plasma for 22nm Technology Node and Beyond**, ***A. Ranjan***, *S. Voronin, H. Kintaka, K. Kumar, P. Biolsi,* Tokyo Electron Technology Center, America, LLC*, R. Jung, S. Kanakasabapathy,* International Business Machines – Research Group*, A. Banik*, IBM T.J. Watson Research Center

Moore's law dictates continuation of shrinkage of transistors to make smaller, faster and less power-consuming devices at lower cost. FinFET (3-D) devices are needed to continue Moore's law. Anisotropy and selectivity requirements in FEOL etches (e.g., FinFET gate) are becoming very demanding and conventional RF plasma sources are hitting their limits to achieve such requirements. Microwave power delivered through radial line slot antenna generates over-dense evanescent microwave plasma just below top dielectric plate, and the electrons cools down (1eV or less in wafer region) due to inelastic collisions with the background gas. Low electron temperature (*Te*), low self-bias (Vdc) and low plasma potential in evanescent microwave plasmas enable "soft" etching for the 22nm generation and beyond technology nodes. In this study, Si-gate etching was performed in a evanescent microwave plasma system to achieve high selectivity over silicon oxide and silicon nitride with vertical profile. In addition to low self-bias, low *Te* is required to obtain high Si selectivity over SiO2 due to low-dissociation of by-products in evanescent microwave

plasmas. Re-dissociated by-products (e.g., SiBrx*) pull out O- from SiO2 resulting in loss of Si selectivity over SiO2. Low *Te* (low re-dissociation) also helps with control of iso-nested CD-loading. High ion-flux with low *Te* plasma yields vertical profile of Si independent of aspect ratio and with minimal iso-nested CD-loading. Various other interesting aspects will also be presented.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Research Alliance Teams in Albany, NY 12222. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

8:20am **PS2-TuM2 Tracking Line Width Roughness Improvement during Gate Plasma Patterning**, ***L. Vallier***, *E. Pargon,* CNRS, France*, N. Posseme,* CEA, LETI, MINATEC Campus, France*, L. Azarnouche,* CNRS, France*, S.D. Nemani, C. Rosslee, T. Pham*, Applied Materials Inc.

The effect of line width roughness (LWR) on the performance characteristics of transistor gates becomes problematic as the critical dimension (CD) of the gate decreases. Minimizing the magnitude of LWR in patterned features is becoming mandatory for the next technological nodes and is actually requested by the International Technology Roadmap for Semiconductor. Showing up particularly at 193nm wavelength exposure, the photoresist (PR) LWR is the main contributor to the final LWR measured in silicon gates following plasma patterning; therefore most of the effort is focused on the PR LWR reduction prior to the plasma transfer. At the same time, it was observed that the magnitude of LWR decreased when transferred from resist into the gate material. Plasma action might further help in the LWR reduction. In this work we have implemented the Power Spectrum Density (PSD) method as a measure of the LWR spatial frequencies distribution of a line, to monitor its evolution during the patterning of silicon gates with plasma etching process, starting from the PR after lithography up to the Silicon gate line. Thanks to the PSD method, noise coming up from CD SEM pictures of PR lines acquired at very low electron fluency can be subtracted, enabling a real LWR measure of the line with associated frequencies. A robust protocol for the CD SEM data treatment was developed and applied to various process conditions, aiming to obtain the best LWR reduction. Several cure treatment of the PR, achieved prior to the plasma etching of the gate, were investigated with the combination of UV light, plasma exposure using different gas chemistries, thermal treatment, pulsed plasma and E-beam exposure. This work confirms that the etch process can reduce the magnitude of roughness in silicon over a range of mid and high spatial frequencies, that is smoothing the line, however the extent of this roughness reduction vanishes as the resist LWR reaches its minimum. These results demonstrate that plasma action during the gate etch cannot improve the LWR much and post-etch LWR in silicon may be limited by the minimum LWR achievable in resist, therefore pushing for efficient PR cure treatment where plasma exposure play a key role. Based on the PR material used in this study which presents a 6.5 nm initial LWR value after lithography, a LWR of 2.9 nm was measured after the best LWR reduction process highlighting the need for further improvement to match the LWR requirement of the next technological nodes.

8:40am **PS2-TuM3 Plasma Prize Talk: Grand Challenges in Etch**, *R. Gottscho********, **S. Sriraman***, Lam Research **INVITED**

Plasma etching has enabled the perpetuation of Moore's Law from >1 um to now less than 20 nm. More than ever, plasma etching is used to enable the extension of semiconductor device fabrication into the nanoelectronics age. The industry has always faced etch challenges due to scaling laws, especially as we begin to manufacture features that require atomic etch precision. Etch precision is especially challenging as the industry moves to 3D architectures, as we are etching electrically active layers in structurally complex features. Also, though we've always had to etch high aspect ratios, the fundamental challenge of aspect ratio dependent etching is now through alternating thin materials. The additional challenge to control wafer edge effects and reduce cost of consumables is ever more critical with compounding effects of multiple passes needed to compensate for lithographic limitations. In this presentation, I will give an overview of where we currently stand on our understanding of the origins and some solution approaches to the grand challenges in etch.

* 2011 Plasma Prize Winner

9:20am **PS2-TuM5 Spacer Patterning for Trigate SOI Devices***, **S. Barnola**, P. Pimenta-Barros, L. Desvoivres, J. Pradelles, S. Barraud*, CEA, LETI, MINATEC Campus, France

Demonstrations of Trigate SOI devices recently reported highlight a better scalability with improved subthreshold slope and immunity to short channel effect for aggressively scaled CMOS Si devices. However, there are several key challenges in these devices to achieve high performance. Extremely narrow and uniform silicon fins are required combined with increased fin pitch in order to improve the effective channel width and then, the drive current. This work aims to demonstrate Si fin pattern with a width of 10nm and a fin pitch of 35nm.It is no possible to create 10nm dense active features by using only 193nm immersion lithography because of its optical limitations. Consequently, several approaches have been developed in order to reach ITRS predictions, such as e-beam lithography, Extreme UV, negative tone development, block copolymer, and Self-Aligned Double Patterning (SADP). Regarding the technical issues that remain to be solved for each approach, SADP is one of the most promising solutions for the 14nm technology node and below.SADP approach includes at least 3 steps (lithography, spacer deposition, spacer and Si etching) to divide by 2 the pitch of the 1st lithography. For practical reasons and for reducing the number of SADP steps, e-beam lithography has been used to create the "mandrel" patterns that support the spacers. The e-beam initial pitch is 70nm, whose CD has to be reduced to 25nm by a trimming step to reach the final 35nm pitch after SADP. The integration scheme investigated in this work includes the following steps: e-beam lithography with trilayer stack, resist trimming, trilayer etching, SiARC removal, spacer deposition, spacer etching and SOC stripping. All plasma etching steps were carried out on 300mm ICP LAM VERSYS.One of the major challenges of this SADP integration was to limit the Si and SiO2 consumption from the SOI substrate during the SADP process steps. We also had to consider the impact of the non-symmetrical spacers on the micro-loading effect during Si etching. Integration scheme with a buffer layer has been investigated to limit the Si and BOX consumption, but this approach makes CD control more complicated. Thus, we have compared the two integration schemes, with and without buffer layer, in term of CD control and profile to achieve the requirements for this FEOL application for SOI technology.

9:40am **PS2-TuM6 Key Challenges in FinFET FEOL RIE Processing at the 14nm CMOS Node and Beyond**, ***R.M. Martin****, A. Banik, J. Chang, R. Jung, S. Kanakasabapathy, M. Kobayashi, Q. Lin, B.G. Morris, S.C. Seo, T. Standaert, K. Stein, R. Sreenivasan, H. Wang, M. Yang, Q. Yang, Y. Yin,* IBM Corporation*, D.H. Choi, R. Kambhampati, T. Kwon*, GLOBALFOUNDRIES

For CMOS nodes at 22nm and below, the gate critical dimensions become small enough so that conventional methods for addressing issues such as short channel effects on planar devices become ineffective. Fortunately, alternative non-planar devices are becoming mature enough so that they can be used at these next generation technology nodes. Development of new processes to build such three dimensional structures present new challenges for both lithography and plasma etching. In this presentation, we will review processes for building finFET devices in the front end of line (FEOL) from a patterning perspective. Below 80nm print pitch, double patterning methods such as sidewall image transfer (SIT) and pitch split can be employed, however, these more complex methods require additional precision in the plasma etching profile and selectivity to avoid issues such as pitch walking and line edge roughness. Furthermore, at these smaller dimensions and with the complication of 3 dimensions, issues such as RIE lag become much more apparent. Challenges such as these, and some of their potential solutions will be discussed.

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

10:40am **PS2-TuM9 Patterning Options for 14nm Node and Beyond***, **Y. Yin**, R. Jung, F. Lie, M. Beard, B.G. Morris, M. Hartig, S. Kanakasabapathy,* IBM Res. at Albany Nanotech*, Y. Mignot,* STMicroelectronics*, Y. Xu, C. Koay,* IBM Res. at Albany Nanotech*, L. Jang,* GLOBALFOUNDRIES*, N. Saulnier, J. Abdallah, H. Chen,* IBM Res. at Albany Nanotech*, M. Tagami,* Renesas Electonics*, K. Akarvardar, S. Akarvardar,* GLOBALFOUNDRIES*, J. Arnold, T. Spooner, M. Colburn*, IBM Res. at Albany Nanotech

Beyond the 22nm node, limitations of traditional patterning processes become critical. Conventional 193nm immersion lithography is not able to resolve features below 40nm half pitch with a single exposure for Front, Middle and Back Ends of Line. Patterning vias at appropriate CD and spacing is equally challenging. Until further wavelength scaling through Extreme Ultraviolet (EUV) the industry's attention is focused on Double Patterning. Pitch Splitting (PS) Lithography and Sidewall Image Transfer (SIT) are the two broad categories of techniques that have been under evaluation for sub-22nm nodes. Moreover, as we keep shrink the key features to dimensions of interest to sub-14nm nodes, innovations on

existing double patterning techniques and the introduction of emerging patterning techniques such as directed self-assembly are needed in order to enable sub-40nm pitch features patterning. In this talk we will address the innovations further needed on existing double patterning methods and discuss the opportunities and challenges of emerging advanced patterning techniques in order to meet the patterning requirements for 14nm node and beyond.This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:00am **PS2-TuM10 High-Efficiency Downstream Plasma Processes**, ***L. Diao***, *R. Elliston, A. Kadavanich, C. Lee, V. Nagorny, H. PhanVu, O. Todor, V. Vaniapura*, Mattson Technology

Photoresist (PR) strip processes continue to improve with major IC technology node advances and architecture changes. One of the new technologies currently being implemented for the 2x nanometer node, high-κ metal gate (HKMG) has emphasized the need for enhanced reducing chemistry processes, which are also widely used in other strip-over-metal applications. Three-dimensional vertical architectures present great challenges for high aspect ratio (HAR) processing, and stacked structures often require low-temperature process capability. Control specifications for critical processes are further tightened as more new materials are introduced at advanced geometries. Industry-wide strip process enhancements have diverged into two directions: increasing RF power or adding bias. In either case, wafer surface temperature increases significantly, which introduces pattern damage. Furthermore, there is increased risk of plasma-induced damage (PID). A new Mattson Technology dry strip source provides a solution to these challenges.

Based on the company's proprietory Faraday-shielded inductively coupled plasma (ICP) source technology, the new source offers these distinctive features: (1) a specially designed plasma generation volume with improved electron confinement that provides high efficiency of electron heating and enhanced plasma stability, and (2) a gas injection system that directs all the gas flow through this volume to increase efficiency of gas utilization. This results in efficient use of process inputs (power, gases) while simultaneously widening the operational window in terms of pressure, power, temperature.

The new source demonstrated significant increase of the PR removal rate and reduction of non-uniformity across different chemistries. One major benefit was observed with pure reducing chemistry. The new source with high power nearly doubled the ash rate, at 20% H2 in N2 with non-uniformity of <5%. Its impact on critical dimension (CD) and sheet resistance (Rs) were minimum and enabled better strip over metal process. O2-rich reducing chemistry with high power was used in HAR PR removal in the middle-end-of-line (MEoL) contact container. It showed improved residue removal capability with challenging AR. One more time, Rs was well controlled over exposed metal liner with high power. CF4-containing chemistry for amorphous carbon hard mask removal demonstrated improved productivity and selectivity over oxide and nitride at extremely low temperatures. Avoiding high power usage, the enriched reactant species allow HDIS process with dry only residue free, less pattern damage, lower silicon (Si) loss and controlled oxidation with different chemistries.

11:20am **PS2-TuM11 Challenges for Sub 20nm STI Etch**, ***H. Zhou***, *X. Ji, S. Srinivasan, J. He, X. Hua, D. Heo, J. Choi, A. Khan, A. Agarwal, S. Rauf*, Applied Materials Inc.

With the feature size scaled down below 20nm, the plasma etching technology for shallow trench isolation (STI) becomes very challenging. The aspect ratio of the isolation trench can be as high as 20:1, and the space CD variation from double patterning is no longer negligible. Advanced processes and hardware are then required for the sub 20nm STI etch to minimize the depth loadings, i.e. intra-cell loadings. First approach is to trim the mask at the beginning to reduce the aspect ratio of the mask. With trimmed mask, the intra-cell loading is reduced. Second approach is realized with pulsed plasma. The period of pulsed plasma is ~ms, which is comparable to the residence times of typical plasma etch conditions. During the off cycle, the radicals/ions/byproducts have extra time to move out of the trench or act on the sidewall independently, and the sidewall polymer deposition is better managed. The advantage of pulsed plasma has been demonstrated with both 13MHz and 2MHz bias frequencies. Synchronized pulsed plasma etching has shown at least 40% improvement on CD-dependent depth loading than continuous wave plasma process. Moreover, 2MHz bias frequency also helps to round the trench bottom with higher energized ions. Another challenge for sub 20nm STI etch is profile control at extreme edge. Because of the plasma sheath bending effect, extreme edge trenches tend to tilt toward the wafer center. This issue can be fixed with a novel improvement of bottom electrode, which also improves the depth uniformity across the wafer. The ion flux with the novel bottom electrode is more uniform, in particular at the extreme edge locations. Compared to the standard electrode, the center to extreme edge trench depth variation has been reduced from 14.55% to 4.42% with the novel bottom electrode. Challenges for sub 20nm STI etch also include in-situ etching and line bending prevention, which will be also discussed.

Advanced Surface Engineering
Room: 22 - Session SE+PS-TuM

Pulsed Plasmas in Surface Engineering
Moderator: C. Mitterer, University of Leoben, Austria

8:00am **SE+PS-TuM1 Strong Localization of Ionization in High Power Impulse Magnetron Sputtering in Reactive and Non-Reactive Gas Environments**, ***A. Anders***, Lawrence Berkeley National Laboratory **INVITED**

Self-organized structures of plasmas in high power impulse magnetron sputtering (HiPIMS) have recently been observed by several groups. The structures move along the racetrack in the ExB drift direction but only with about 10% of the electron drift velocity (E and B are the electric and magnetic field vectors). The bright structures are zones of concentrated ionization: they can be related to the amplification mechanism of self-sputtering and gas recycling. The ionization zones can readily be observed with fast cameras providing time resolution of 1 microsecond or better. The situation will be illustrated with images taken with a gated intensified frame image camera (Princeton Instruments) and with an intensified streak camera (Hamamatsu). Both end-on and side-on views to the magnetron are utilized. The side-on view reveals that each dense ionization zone is associated with an electron beam leaving the target region. Such beam maintains the quasi-neutrality of the plasma as ions are "evacuated" towards the target. The motion of the ionization zones is not a motion of plasma but a displacement of the region of greatest ionization. Its speed is mainly limited by the inertia of ions. The mechanism will be discussed and supported with images taken for various targets in noble and reactive gas atmospheres. Finally, the consequences of the localization of ionization for film formation will be considered in the greater context of energetic condensation.

8:40am **SE+PS-TuM3 The Magnetic Field Configuration's Effect on Plasma Parameters in High-Power Pulsed Magnetron Sputtering**, ***H. Yu***, *L. Meng, P. Raman, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

Magnetic field design is crucial in DC magnetron sputtering operation, but has been largely overlooked in high power pulsed magnetron sputtering (HPPMS). In a HPPMS discharge, plasma disperses after each short pulse, unlike in the DC operation which requires a good magnetic confinement to maintain the plasma. It is thus interesting to study the effect of magnetic field configuration on HPPMS discharge for further optimization. A special magnet pack was fabricated with the magnet positions fully adjustable. Different designs were made, with the corresponding magnetic field calculated by Comsol. For example, the magnetic field (B) strength in the racetrack was varied, as 200, 500, and 800 Gauss. Different racetrack shapes were used, such as ring-like and bean-like. Designs were also made to have incomplete racetrack, and weak racetrack in which piles of magnets were placed evenly across the whole pack and polarities of adjacent piles were opposite. These magnetic configurations were then tested in a large magnetron system with a 36 cm target using a conventional HPPMS plasma generator. The I-V discharge characteristics were measured. A time-resolved triple Langmuir probe was employed to study the temporal evolution of electron temperature (T_e) and density (n_e) across the substrate. Ionization fractions of sputtered metal were also measured using quartz crystal microbalance combined with electrostatic filters. The results showed that higher B field strength and longer racetrack produced higher pulse current. The 500 Gauss configuration however had higher n_e in the pulse than 800 Gauss did, likely because it allowed easier plasma diffusion. In all the designs with a racetrack, the distribution of n_e on the substrate was non-uniform that n_e was typically about 10 times higher right below the racetrack than at the center. The weak racetrack configuration was found to work and showed certain superiority over the normal DC magnet design. The plasma was generated from almost the entire target surface indicating an improvement in target utilization without the need for rotation. The discharge current was comparable with the racetrack designs. Furthermore, the plasma density distribution over the substrate was very uniform.

9:00am **SE+PS-TuM4 Plasma Generation and Transport in High-Power Pulsed Magnetron Sputtering**, ***L. Meng***, *H. Yu, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

High power pulsed magnetron sputtering (HPPMS) processes, including its potential application in interconnect metallization during microfabrication, require a precise control of fluxes and energies of various plasma species. A more fundamental understanding of the pulsed discharge mechanisms and

the underlying physics thus becomes necessary. In a 36 cm planar magnetron system, a triple Langmuir probe was used to study the time-resolved behaviors of the HPPMS plasma under various discharge and pulsing parameters, as well as at different positions extending from the target surface. The pulsed plasma was shown to be established through multiple stages. And the 3-dimensional probe characterization depicted a scenario of plasma expansion from the plasma-confined racetrack, producing high density peaks up to 10^{19} m^{-3} into the pulse-off period. The delay time of these peaks from the pulse-off edge varied from several to several hundred µs with different probe positions, and was found to depend on the plasma density in the racetrack which affects the diffusion constant, and the temporal location of the peak plasma density in the racetrack as well. In addition to the probe measurements in the vicinity of the racetrack, a special setup with quartz crystal microbalance and current collecting plate behind orifices drilled in the target was designed. Ion fluxes to the cathode were directly measured, while the metal ion and argon ion fluxes were distinguished time-averagely. The self-sputtering theory of HPPMS is supported by a higher metal ion fraction measured at a higher pulse peak current. Based on the above experiments, a 1-dimensional time-dependent HPPMS discharge model was developed incorporating the surface reactions, ionization process in the plasma, and plasma diffusion. It was able to describe the essential processes of plasma buildup and dispersion, and to predict some important plasma properties such as density and ionization fraction from the basic inputs of magnetic field, discharge and pulsing parameters, etc.

9:20am **SE+PS-TuM5 Metallic Film Modification through the Use of Non-standard HiPIMS Waveforms**, *P.M. Barker, E. Lewin,* ***J. Patscheider***, EMPA, Switzerland

High power impulse magnetron sputtering, HiPIMS, has been the source of significant scientific interest in recent years. HiPIMS consists of a high voltage / high current pulse, followed by a long off-period resulting in low duty cycles. In the present study additional control parameters are explored by using non-standard HiPIMS waveforms, consisting of pulse sequences. These pulse sequences consist of a number of micro-pulses, which can be varied in length. In a further novel approach to HiPIMS, the pulses were also applied in a bi-polar manner, with a positive voltage supplied to the same target between negative voltage pulses. Films have been grown using varied pulse sequences, in both uni- and bi-polar mode, and compared to materials grown both by traditional, single pulse, HiPIMS and dcMS.The deposition of Ti metal was chosen as a model system, and the attained coatings were analysed using X-ray diffraction, XRD, scanning electron microscopy, SEM, and X-ray photoelectron spectroscopy, XPS. An increased deposition rate, relative to a comparable standard HiPIMS pulse, was observed. The coating microstructures show increased smoothening of the coating surface and shallower surface oxidation for samples deposited using micro-pulsed HiPIMS.

10:40am **SE+PS-TuM9 Reactive Modulated Pulse Power Magnetron Sputtering of Molybdenum Oxides: Optical Behavior as a Function of Process Parameters**, ***N.R. Murphy***, Air Force Research Laboratory, *L. Sun,* General Dynamics Information Technology, *J.T. Grant,* University of Dayton Research Institute, *J.G. Jones, R. Jakubiak*, Air Force Research Laboratory

Molybdenum oxide, a material prized for its ability to facilitate thermochromism and electrochromism, has displayed considerable sensitivity to oxygen concentrations present during reactive DC magnetron sputtering. Typical depositions performed using continuous reactive DC magnetron sputtering have demonstrated low deposition rates and limited control over stoichiometry as a result of oxygen induced target poisoning. In the following study, molybdenum oxide films were deposited using reactive modulated pulse power magnetron sputtering (MPPMS) using a 99.999% pure molybdenum sputtering target within an argon-oxygen atmosphere. At a pressure of 10 mTorr, the oxygen concentration was varied between 1 and 20%. The resulting films were characterized by way of in-situ spectroscopic ellipsometry, x-ray photoelectron spectroscopy, x-ray diffraction and UV-visible spectroscopy. The as-deposited films were determined to be amorphous by way of x-ray diffraction analysis and were analyzed without any prior heat treatment. *In-situ* spectroscopic ellipsometry was conducted throughout the deposition process, monitoring real time changes in the refractive index, extinction coefficient and thickness of the film.

11:00am **SE+PS-TuM10 Cathodic Arc Plasma of AlCr Composite Cathodes in Inert and Reactive Atmospheres**, ***R. Franz***, *J. Wallig,* Lawrence Berkeley National Laboratory, *P. Polcik,* PLANSEE Composite Materials GmbH, Germany, *A. Anders*, Lawrence Berkeley National Laboratory

In the past, the distributions of ion charge states of vacuum arcs have been studied in great detail under various conditions, including their dependence on arc current level, strength of a magnetic field (if present), pressure and kind of background gases, and the distance from the plasma-producing cathode spots. Most of the work was done using pure elementary cathodes since the presence of two or more elements in the cathodes would most likely further complicate the situation when studying the physics of cathodic vacuum arcs. However, in many practical applications ternary or quaternary thin films are used. For their synthesis it is common to employ composite cathodes consisting of the elements of interest.

In the field of hard and wear-resistant coatings, thin films based on the system aluminium and chromium represent the state of the art. With the addition of nitrogen and/or oxygen ceramic coatings covering a wide compositional range can be synthesised. In the present study, a time-of-flight spectrometer was used to investigate the arc plasma composition in terms of elemental and ion charge state composition when using Al_xCr_{1-x} ($0 \leq x \leq 1$) composite cathodes in different gaseous environments, i.e. in vacuum as well as argon, nitrogen and oxygen atmosphere. The observed ion distributions were interpreted in the established framework of plasma generation at cathode spots and ion-gas interactions.

Plasma Science and Technology
Room: 24 - Session PS1-TuA

Plasma Deposition and Plasma Enhanced ALD
Moderator: S. Agarwal, Colorado School of Mines

2:00pm **PS1-TuA1 Looking Down the Rabbit Hole: Impact of Porosity in Plasma-deposited Inorganic Layers on Their Moisture Permeation Barrier Performance**, ***M. Creatore***, Eindhoven University of Technology, The Netherlands **INVITED**

Although very promising results in terms of moisture and oxygen permeation barrier properties have been achieved by organic/ inorganic multi-layers, the impact of the organic interlayer on the global barrier performance is still under discussion. It is generally considered that the organic interlayer acts as smoothening layer for the macro-defects present at the surface or in the barrier layer. It is also hypothesized that the organic interlayer infiltrates into the nano-pores present in the barrier layer, therefore affecting the barrier itself at microstructure level.

In the present work the moisture permeation barrier performance of multi-layers deposited by means of initiated- and plasma enhanced- CVD methods [1] is addressed, with the aim of unraveling the role of the organic interlayer. Calcium test measurements allowed discriminating between the water permeation through the macro-defects/pinholes and the permeation through the matrix porosity. It has been found that the improvement in terms of barrier properties, due to the filling/infiltration of the SiO_2 layer nano-pores by an organosilicon interlayer [2], universally correlates with the residual open micro- (i.e. < 2 nm) porosity in the inorganic (SiO_2 or Al_2O_3) layer, independently of the deposition method (PECVD or plasma-assisted ALD). The residual nano-porosity has been evaluated by means of ellipsometric porosimetry which allows carrying out adsorption/desorption isothermal of a probe molecule in the open porosity. In detail, only for WVTR values of the SiO_2-*like* layer larger than 10^{-3} g m^{-2} day^{-1}, a barrier improvement factor is observed upon deposition of the organic interlayer, although limited to values between 5 and 10. This outcome, in combination with the evaluation of the macro-defect density upon organosilicon layer deposition on the SiO_2 layer, provides the evidence that smoothening plays a major role in the improvement of the barrier performance.

Next to the growth and characterization studies of the organosilicon/SiO_2 multi-layer, the control on the residual open nano-porosity of high growth rate roll-to-roll atmospheric pressure plasma deposited SiO_2 layers is addressed. Upon 2 nm thick Al_2O_3 layer deposition, the water vapor transmission rate of the SiO_2 layer decreases of a factor 10^3, due to the filling of the residual SiO_2 nano-porosity.

[1] G. Aresta, J. Palmans, M.C.M. van de Sanden, M. Creatore, (2012), accepted for publication in J.Vac. Sci. Technol.

[2] G. Aresta, J. Palmans, M.C.M. van de Sanden, M. Creatore, (2012), Microporous and Mesoporous Materials 151, 439.

2:40pm **PS1-TuA3 Dual Etching and Deposition Mechanism of a Microwave Alcohol Plasma on Commercial Polymers for the Enhancement of Adhesion**, ***C.J. Hall***, *P.J. Murphy, H.J. Griesser*, University of South Australia

The use of polymers to replace traditional materials in the automotive, aerospace and other industries is continuing at a high pace. Polymers offer distinct advantages over glass and metals, such as weight, impact strength, and the ability to be formed into complex shapes. To ensure long service life, however, in some applications the polymers must be coated to provide protection from damage due to mechanical abrasion or chemical attack.

One such protective coating currently being developed is a microwave based PECVD coating using tetramethyldisiloxane (TMDSO) and oxygen. This system can be used to deposit an amorphous siloxane coating several microns thick, at industrially relevant speeds. PECVD has high deposition rates with no cure required; it can coat complex parts and has the ability to vertically grade the composition of the coating. These siloxane coatings can provide the polymers with protection from in-service wear and chemical attack. However, traditionally, adhesion of these coatings to many polymers has been marginal.[1]

In this study it has been found that plasma pre-treatments using vapours from the alcohol family are effective at modifying the adhesion of these coatings to five commercial polymers, polycarbonate (PC), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS). We have observed that the plasma pre-treatment both etches the polymer and deposits a carbonaceous film some 10 to 20 nm thick. It has also been established that both of these mechanisms are required to improve adhesion. Of further interest is the observation that the pre-treatment time must be tailored depending on the polymer substrate. Optimum adhesion is only achieved after some critical time. For ABS and PS, less than 15 secs is adequate, however for polymers, such as PMMA and PC, treatment times up to 120 and 180 secs are necessary. The duration of pre-treatment appears to be related to the etch rate of the particular polymer. Investigation has revealed that the alcohol plasma creates hydroxyl radicals.[2,3]These radicals are capable of initial hydrogen abstraction from the polymer; however, the subsequent etching proceeds depending on the structure of the polymer. As such there is a need to tailor the pre-treatment time depending on the polymer being treated.

1. B. W. Muir, H. Thissen, G. P. Simon, P. J. Murphy, H. J. Griesser, Thin Solid Films **2006**, 500, 34.

2. C. Hall, P. Murphy, H. Griesser, *Plasma Process. Polym.* **2012**, *Accepted, In Press*, DOI: 10.1002/ppap.201100159.

3. C. Hall, P. Murphy, H. Griesser, *Plasma Process. Polym.* **2012**, *Accepted, In Pres.*

3:00pm **PS1-TuA4 The Roles of Ions and Neutrals in Growth Mechanisms of Plasma Polymer Films**, ***A. Michelmore***, University of South Australia

Plasma polymers have been used since the 1960s and have found a wide range of applications. However the basic processes and mechanisms leading to plasma polymer film growth are poorly understood. Due to this lack of understanding, external parameters such as RF power and monomer flowrate are typically quoted in the literature, which provide no information on processes at the molecular level. Therefore reproducing films with different reactors is usually done by trial-and-error as the critical parameters determining growth processes are largely unknown.

Here we will discuss the roles of ions and neutrals in contributing mass to the film with a view to understanding the molecular processes by which plasma polymer films grow. The pivotal role of monomer chemical structure, specifically sites of unsaturation, in determining which growth mechanisms dominate will also be demonstrated.

4:00pm **PS1-TuA7 Defect Analysis and Mechanical Performance of Optoelectronic Thin Films Deposited on Flexible Substrates**, ***R. Patel***, *C.A. Wolden*, Colorado School of Mines

Plasma deposition enables synthesis of optoelectronic thin films on flexible substrates at low temperature. The ultimate performance of these materials is controlled by defects such as pinholes or cracks. This work focuses on understanding the formation of such defects during both film synthesis as well as during the application of stress. A simple solvent-etch based technique is presented which can be used to visualize and quantify defects in both single and multi-layered films deposited on flexible substrates. This approach allows for quantitative evaluation of crack/defect density evolution. This technique is applied to both sputtered indium tin oxide (ITO) as well as alumina-silicone nanolaminates deposited on flexible polycarbonate films by plasma-enhanced chemical vapor deposition. The use of the nanolaminate architecture is shown to significantly attenuate pinhole density relative to single layers. In the case of sputtered ITO, an optimum thickness is identified that balances electronic performance with mechanical integrity. For both materials their performance under applied stress was examined using an automated bending test setup that explored mechanical failure as a function of applied strain and number bending cycles. The threshold strain for failure under the application of tensile/compressive stress was quantified by bending samples to a given radius of curvature. Below a critical strain these materials demonstrate robust performance during cycling, displaying their strong potential for device applications.

4:20pm **PS1-TuA8 Plasma Polymerization of Ethyl Lactate**, ***S. Ligot***, University of Mons, Belgium, *F. Renaux*, Materia Nova Research Center, Belgium, *L. Denis*, University of Mons, Belgium, *D. Cossement*, Materia Nova Research Center, Belgium, *P. Dubois, R. Snyders*, University of Mons, Belgium

Biodegradable and derived from renewable resources, polylactide (PLA) has gained enormous attention as an alternative to conventional synthetic packaging materials. Nevertheless, PLA presents high water and gas permeability, which leads to a high degradation rate by hydrolysis of the

ester bonds and therefore substantially limits its application for food packaging.

In order to improve the barrier properties of PLA substrate, we propose to cover it with a highly cross-linked PLA-based plasma polymer film (PPF) synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD). The control of both chemical composition and cross-linking degree would allow to tune the gas permittivity and, as a consequence, the degradation rate of the PLA substrate.

The present work reports on the study of the influences of the experimental parameters (RF power, working pressure and precursor flow rate) on the PPF films properties using a design of experiments tool. The PPF are studied in terms of chemistry and cross-linkage by XPS, FTIR spectroscopy and Tof-SIMS measurements. In addition, *in-situ* IR spectroscopy is used to probe the plasma in order to get a better understanding on the plasma-surface interactions during the growth process. It comes out that, in our conditions, the applied power is the key parameter controlling the PPF properties. By increasing it, the C/O ratio in the coatings increases from 2.5 to 9.3. The decrease of the oxygen content when applied power is increased is correlated with the loss of O-C=O and C-O functions from 15% to 0 % and from 21% to 5 %, respectively. The *in situ* FTIR data support this observation and suggest the formation of alkynes in the plasma.

4:40pm **PS1-TuA9 Functional Carbon Contained Film Formation using Neutral-Beam-Enhanced Chemical-Vapor-Deposition by Microwave Plasma**, ***Y. Kikuchi,*** Tohoku University and Tokyo Electron, Japan*, A. Wada, S. Samukawa*, Tohoku University, Japan

Carbon materials possess various functional properties by forming various structures of carbon atoms. Especially diamond-like carbon (DLC) film is one of the primary materials as alternative of metal electrodes in various devices, in contract a carbon doped silicon oxide (SiCOH) is known as a low-*k* dielectric in ultralarge-scale integration (ULSI) devices . However, it is difficult to precisely control their properties using conventional plasma-enhanced chemical vapor deposition (PECVD). To solve this problem, we have developed a neutral-beam-enhanced chemical vapor deposition (NBECVD) process as an alternative to the conventional PECVD process. NBECVD can almost completely eliminate the irradiation of UV photons and electrons to the substrate surface by a carbon aperture, resulting in a damage-free deposition process. Moreover, the NBECVD can form a film through surface polymerization caused by bombardment of an energy-controlled Ar neutral beam on the surface with absorbed precursors. We previously proposed controlling the molecular-level structures in SiOCH film on 2 inch wafer by using NBECVD process, which can control the film properties (*k*-value and modulus). Since the bombardment energy of the neutral beam can be precisely controlled by Ar plasma above a carbon aperture, selective dissociation of weak chemical bonds in the precursors is possible with applicable plasma source, which enables us to design the film structure by controlling the precursor structure.

In this study, we developed NBECVD equipment for 8 inch wafer selecting microwave plasma source and deposited DLC and SiCOH films. For DLC film, we used toluene as precursors to control sp^2/sp^3 bonds ratio and hydrogen content in the film. DMOTMDS was selected for SiCOH film as reported previously. As the results, we can form high-quality DLC films and high density and low-*k* SiCOH films on 8 inch wafer by controlling the film structure precisely.

5:00pm **PS1-TuA10 Nano-crystalline Silicon Deposition using a Layer-by-layer Technique**, ***Z. Chen****, M.N. Iliev, J.A. Mucha,* University of Houston*, Y.K. Pu,* Tsinghua University, China*, D.J. Economou, V.M. Donnelly*, University of Houston

Nano-crystalline silicon was deposited using a layer-by-layer technique in a novel reactor with two separate reaction regions for amorphous silicon deposition and nano-crystallization. Substrates were rotated between two internal plasma sources, with selectable processing times in each source. A capacitively-coupled plasma (CCP) with SiH_4/He feed gas was used to deposit thin hydrogenated amorphous Si layers that were then immediately exposed to a H_2 or D_2 inductively-coupled plasma (ICP). The reaction of H or D atoms induced crystallization in the films. With 2 or 4 substrates on opposite sides of a circular susceptor, one substrate was in the SiH_4 CCP, while another was in the H_2 or D_2 ICP. These two processes were performed sequentially and periodically to grow thin films. Raman spectroscopy was used to characterize the films and determine the fraction of crystalline (510 and 520 cm^{-1} peaks) material in the a-Si:H layer (480 cm^{-1} peak). For the same total exposure times in each plasma, nearly the same total thickness films were deposited. Many short exposures to both plasmas were more effective in producing nano-crystalline Si than with one long exposure to each plasma. In addition, the fraction of nano-crystalline Si increased with increasing ratio of H_2 ICP-to-SiH_4/He CCP exposure time. Mass spectrometry was also used to monitor products produced in the D_2 plasma. During crystallization, etching was observed and SiD_xH_y peaks were detected, with the strongest coming at m/e=32 (SiD_2^+, SiH_2D^+). These signals decayed to a small background over times that depended on the exposure time in the SiH_4/He CCP. The films were also characterized by spectroscopic ellipsometry and Fourier transform infrared absorption. By utilizing these characterization methods, the kinetics for crystallization was investigated and will be discussed.

5:20pm **PS1-TuA11 Role of PEALD Reactor Wall Conditions on Radical and Ion Substrate Fluxes**, ***M.J. Sowa****, M.J. Sershen, G. Sundaram, J.S. Becker*, Cambridge NanoTech, Inc.

Plasma Enhanced Atomic Layer Deposition (PEALD) relies on plasma generated species as co-reactants for one half of the cyclic, two-step deposition process. Plasma generated species include radicals, ions, electrons, and photons. PEALD research is still in its early stages and the community is just beginning to elucidate the roles of these species in the deposition process and ultimately in the resulting deposited film characteristics.

Plasmas can exhibit quite complex behavior. Without excellent Faraday screening, Inductively Coupled Plasmas (ICPs) will have some component of capacitive coupling between the induction coil and the plasma. This leads to various amounts of extension of the "remote" plasma into the ALD reactor as currents originating at the high capacitive potentials of the plasma source seek out a grounded counter electrode. The sink location for the capacitive currents would be expected to vary substantially depending on if the ALD reactor is coated with a conducting or insulating film.

Ideally the plasma source will deliver a high flux of radicals to the substrate surface. Recombination of radicals on reactor wall surfaces is one of mechanisms by which the radical flux is reduced between the remote source and the substrate. The wall/radical recombination rate is a function of the radical species, the wall material, and the wall temperature.

In a PEALD system which sees multiple film chemistries, at any given time the exposed coating on the reactor walls may be of various conducting or insulating materials. The plasma properties and the radical recombination properties, and thus the flux and characteristics of plasma generated species seen by the substrate, could be substantially different depending on the details of the wall films. Additionally, the wall characteristics could change during the deposition leading to drift in the process over the course of the deposition. This, is turn, could lead to within wafer and wafer-to-wafer non-uniformities.

We have investigated the role of various insulating and conducting wall films on the spatial radical flux and spatial ion flux and energy distribution. Measurements were made on multiple ICP sources designed to deliver radicals to a PEALD reactor in a remote plasma configuration. Measurements were made over a range of rf powers (50-300W), gas compositions (Ar, O2, N2, and mixtures), gas flow rates (10-400sccm), wall films (304L SS, Al2O3, Pt, …), wall temperatures (RT - 200C), and probe/plasma source distances (150 - 450mm). Relative radical flux measurements are derived from the mass loss of photoresist coated QCM crystals. Ion data are derived from Langmuir probe measurements.

5:40pm **PS1-TuA12 Tuning Material Properties in ALD ZnO Films: *In Situ* Plasma Treatments and Doping**, ***M.A. Thomas,*** Stetson University*, J.B. Cui*, University of Arkansas at Little Rock

A variety of techniques has been used to modulate the material properties of atomic layer deposited (ALD) ZnO thin films. The structural, optical, and electrical properties of the various ZnO films were characterized by techniques such as scanning electron microscopy, atomic force microscopy, x-ray diffraction, photoluminescence, transmission/absorption, and resistivity and Hall effect measurements. The electrical properties of ALD ZnO are shown to be readily tunable by combining in-situ plasma treatments with standard thermal-ALD processes. This new ALD technique is labeled plasma enhanced thermal-ALD (PET-ALD) and is capable of significantly reducing or increasing the *n*-type conductivity in ZnO by employing either an O_2 or H_2 plasma, respectively. The resistivity of such PET-ALD films is controllable within more than seven orders of magnitude. Doped ZnO films are also readily obtained by inserting an appropriate number of dopant cycles in between the standard ZnO growth sequence. By adjusting the number of dopant cycles the optical and electrical properties of ZnO can also be well controlled. These ALD films possessing a wide range of structural, optical, and electrical properties, all of which can be easily tuned with appropriate deposition parameters, serve as excellent candidates for use in a variety of electronic and optoelectronic devices.

Plasma Science and Technology
Room: 25 - Session PS2-TuA

Plasma Surface Interaction during Plasma Etching
Moderator: S. Shannon, North Carolina State University

2:00pm **PS2-TuA1 Surface Interaction Mechanisms Enabling Plasma-Enhanced Strongly Time-Dependent Etching Rates**, ***D. Metzler***, *E. Vogli, F. Hilpert, G.S. Oehrlein*, University of Maryland

There is great interest in establishing directional etching methods capable of atomic scale resolution during fabrication of highly scaled electronic devices. We report a new concept to achieve controlled, self-limited etching of extremely thin layers of material using a polymer as a special case. The work was performed in a capacitively coupled plasma reactor. The polymer material is a 248nm photoresist. A complete process cycle consists of: O_2 exposure of the polymer material, exhaust of O_2 from the chamber, low energy Ar^+ ion bombardment of the surface using Ar plasma to remove the oxygen-bonded carbon species, and Ar exhaust. This sequence is repeated up to 20 times to investigate reproducibility of each cycle and time dependent behavior. Controlled etching is based on deposition of a thin reactive layer during Ar^+ sputtering from a polymer-coated electrode (polyimide-related material) within the chamber. The polyimide-related film deposition balances etching during the Ar^+ ion bombardment step once the reactive layer has been removed, and enables control of the etching depth. Ar^+ ion bombardment energies were selected so that once the oxygen-bonded carbon material and physisorbed layer had been removed, net etching ceased. If the ion energy is too small, deposition of sputtered polyimide-related material dominates over etching. When applying a too high selfbias voltage, significant pristine polymer etching takes place and a self-limited process cannot be achieved. Using real-time ellipsometric monitoring, we demonstrate strongly time-dependent etching rates. Starting with a high etch rate of ≈19 nm/min for 2 sec, it decreases within the next 5 sec to 0 nm/min, and therefore shows self-limitation. During the Ar etching step, the O_2 modified deposited reactive layer along with 0.13 nm unmodified polymer can be removed, while concurrent deposition prevents net etching of the unmodified polymer and enables achievement of self-limited etching cycles. This etch is believed to be d irectional enabled by the energetic ion bombardment of the surface. Subsequently, the reactive surface is modified by O_2 adsorption during the O_2 exposure step. Molecular oxygen does not spontaneously react with carbon-based polymers at room temperature, but can be adsorbed on an activated polymer surface to form a very thin layer of oxidized carbon material over unmodified polymer. A thickness increase of 0.6 nm per cycle is observed via real-time ellipsometry. Additional XPS studies allow the investigation of the surface material composition for further insight on the reactive layer deposited during the Ar^+ etching step and the adsorbed layer during O_2 exposure.

2:20pm **PS2-TuA2 Reactive Etching or Deposition Properties of Silicon Halide Ions in Gate Etching Processes**, ***T. Ito***, *K. Karahashi, S. Hamaguchi*, Osaka University, Japan

As semiconductor devices continue to miniaturize, a better understanding of basic reactions of etching and/or deposition processes on substrate surfaces has become more importantthan before for finer controls of device structures in the manufacturing processes. In typical gate etching processes by halogen plasmas (such as HBr plasmas), Si atoms that are desorbed from the substrate surface and enter the plasma may form silicon halide ions (such as SiBr+) or charge neutral radicals (such as SiBr) and serve as additional etchants. For example, silicon halide ions in the plasma may also be accelerated by the sheath voltage and re-enter the substrate surface. They also may interact with the sidewalls and deposit Si there. Therefore Si containing ions and charge-neutral species may affect etching yields and etched profiles.To clarify the roles of such species in gate etching processes, we have examined sputtering or deposition reactions of Si, Si_3N_4, and SiO_2 substrateswith silicon halide ions, using a mass-analyzed ion beam system. The ion beam system allows one to irradiate a sample surfacewith a specific ionic species at a given incident energy under ultra-high vacuum conditions and evaluate the etching yields and surface chemical reactions. The surface chemistry can be examined by in situ X-ray photoelectronspectroscopy (XPS) and desorbed species by the etching reactions can be detected by a quadrupole mass spectrometer (QMS) installed in the vacuum chamber. In this study, etching yields of silicon bySiClx + orSiFx + ion beams were evaluated with incident energies of 500 – 1000 eV. It has been found that, depending on the incident energy, these species tend to deposit Si on the surface although they also simultaneously etch the substrate. Some properties of such etching/deposition processes may be understood from elementary reaction processes of Si deposition and halogen etching.

2:40pm **PS2-TuA3 Cl Atom Reactions on Silicon Oxy-Chloride Layers Deposited on Chamber Walls in Chlorine-Oxygen Plasmas**, ***A.K. Srivastava***, University of Houston, *R. Khare*, Lam Research Corp, *V.M. Donnelly*, University of Houston

The effects of O_2 addition to a Cl_2 inductively-coupled plasma (ICP) on the heterogeneous reactions of Cl atoms during silicon etching has been studied, using the "spinning wall" method with line-of-sight mass spectrometry, optical emission spectroscopy and Auger electron spectroscopy. A cylindrical substrate embedded in the wall is rotated so that its surface periodically passes through the plasma chamber and then through the differentially pumped diagnostic chambers. Langmuir-Hinshelwood desorption products are detected as a function of time after leaving the plasma, established by the variable rotation frequency. A silicon wafer electrode placed inside the plasma chamber was etched for 10 min with -119 Vdc self-bias in a 2.5 mTorr, 400 W Cl_2 ICP, depositing etching products on the chamber walls and spinning substrate. The Si-electrode bias was turned off and the chamber walls were conditioned with a Cl_2 ICP for an hour. A silicon oxy-chloride (SiO_xCl_y) layer of stoichiometry Si:O:Cl = 1:0.38:0.38 was formed, with the O being a result of slow etching of the quartz discharge tube. No significant Cl recombination on this layer was observed (recombination probability, $\gamma_{Cl} < 0.001$). With the addition of 5% O_2 to the feed gas, the Si-wafer was again biased for 10 min to deposit SiO_xCl_y products on the chamber walls, which were then conditioned with a no-bias ICP for another hour, leaving a film with Si:O:Cl = 1:1.09:0.08. Cl recombination was observed on this surface, with $\gamma_{Cl} = 0.03$. No etch products were detected in the mass spectrometer and hence there is no significant etching of the silicon oxy-chloride layer deposited on the chamber walls at this oxygen fraction. On further treating the surfaces with a pure O_2 plasma for 60 min, the surface composition became Si:O:Cl = 1:1.09:0.04. On this surface the Cl-atom recombination was further enhanced, with $\gamma_{Cl} = 0.04$. We attribute this behavior to Cl recombination occurring at chlorinated O sites rather than chlorinated Si sites on silicon oxy-chloride surface, because of the weak Cl-O bond compared to the Cl-Si bond.

3:00pm **PS2-TuA4 Molecular Dynamic Simulation of Possible Damage Formation at Vertical Walls of finFET Devices during Plasma Etching Processes**, ***K. Mizotani***, *M. Isobe, S. Hamaguchi*, Osaka University, Japan

Development of multi-gate field effect transistors (FETs) such as fin-type FETs (finFETs), which can suppress short channel effects, have been considered as a leading approach to continue to follow Moore's law after the current planer MOSFET technologies reach the size limitations. In finFETs, the Si vertical walls are typically designed to function as gate channels and therefore damages at the vertical walls possibly caused by ion bombardment during the gate etching processes must be minimized. During such etching processes, ions may impinge upon the vertical surfaces but their angles of incidence should be nearly grazing angles. Energetic ions at large oblique angles of incidence against the surface are often considered to be less harmful than those with normal angle of incidence if their incident energies are the same. However, a recent study [1] performed by mass-selected ion beam system has shown that H^+ ion injection at 60 degree from the surface normal can form a deep damage later near the substrate surface. In addition, it is known that simultaneously injection of H^+ ions and O atoms cause enhanced surface oxidation on the Si substrate [2]. In this study, we have used molecular dynamics (MD) simulations to study damages caused by ion bombardment with oblique angles of incidence. It has been found in MD simulations that light ions such as H^+ can indeed cause a deep damaged layer near the substrate surface even at large angle of incidence whereas heavier ions such as Br^+ ions cause less damages under the same conditions.

[1] T. Ito, K. Karahashi, K. Mizotani, M. Isobe, S.-Y. Kang, M. Honda, and S. Hamaguchi, Jpn. J. Appl. Phys. (2012) *in press*.

[2] T. Ito, K. Karahashi, M. Fukasawa, T. Tatsumi and S. Hamaguchi, Jpn. J. Appl. Phys. 50 (2011) 08KD02.

4:00pm **PS2-TuA7 Real time *In Situ* Electron Spin Resonance (ESR) Study of Free Radicals on Materials Created by Plasmas**, ***K. Ishikawa***, Nagoya University, Japan, *H. Horibe*, Kanazawa Institute of Technology, Japan, *M. Ito*, Meijo University, Japan, *M. Sekine, M. Hori*, Nagoya University, Japan **INVITED**

Introduction - To understand a mechanism of plasma-surface interaction, there needs analysis of reactions between plasmas and materials. It has long been appreciated that free radicals play important roles for controlling the reactions. The electron-spin-resonance (ESR) technique can detect the radicals - in particular dangling bonds - and thus we have developed methods to utilize the ESR for this purpose [1]. In this study, we focused on ESR detection of free radical on materials interacted with plasmas.

Polymeric materials - An ESR system was connected to a plasma discharge system (2.45 GHz, 50 W) using a quartz tube with an inner

diameter of approximately 9 mm. Gas (H2, O2, etc.) was flowed into the quartz tube and the pressure was maintained at approximately 100 Pa in the downflow region. ESR measurements were conducted using a standard X-band (9 GHz) spectrometer with a microwave resonator. The quartz tube and poly(methyl-methacrylate)(PMMA)-ralted polymer (methacrylic acid, ethylacrylate, ethyl-methacrylate, acrylic acid, etc.) film sample were inserted inside the ESR cavity in the down-flow region, typically 20 cm from the plasma discharge.

During exposure of gaseous radicals on the polymer surface, the *in situ* real-time ESR technique was detected creation of dangling bonds on surface at real time and provided to the microscopic understanding of chemical reactions on surfaces with gaseous radicals during plasma processes. We have successfully obtained information regarding the reaction mechanism with radicals generated by plasma induced surface interactions.

Biological organism - In another, fungal spores of *Penicillium digitatum* were diluted by sterilized water mixed surfactant (Tween 20) for avoiding clump of spores, and then dried it on a quartz plate. ESR observation of the spores was conducted during oxygen plasma exposure.

Decrease of ESR intensity was corresponded with inactivation behavior where no germination of the spores was observed, eg. no sprout on the mycelia after plasma exposure. Through clarification of individual effects of plasma emission lights, neutral and charged species, this behavior is interpreted that intercellar stable free radical such as quinones was destroyed by exposing oxidizing species generated in the plasmas.

Conclusion - The real time *in situ* ESR method has a great potential for analyzing the interactions with materials and plasmas.

Acknowledgments - This study was partly supported by the Knowledge Cluster Initiative (the second stage), Tokai region, MEXT.

1. K. Ishikawa *et al*., J. Phys. Chem. Lett. **2**, 1278 (2011).

4:40pm **PS2-TuA9 Roles of Hydrogen for Hydrofluorocarbon (HFC) Plasma Etching of Silicon Nitride (SiN)***, **S. Hamaguchi**, K. Miyake, K. Mizotani, M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan*, M. Fukasawa, T. Tatsumi*, Sony Corporation, Japan

Silicon nitride (SiN) is a chemical compound widely used in semiconductor devices or their manufacturing processes as, e.g., gate spacers, stress liners, or hard masks for reactive ion etching (RIE) processes. As to RIE processes of SiN, it has been known that the content of hydrogen (H) in a hydrofluorocarbon (HFC) plasma strongly affects the SiN etching rates. The goal of the present study is to clarify the reaction mechanism of SiN etching. Our earlier studies based on molecular dynamics (MD) simulations and ion beam etching experiments suggested that hydrogen in HFC plasma tends to reduce the thicknesses of a carbon-rich surface layer deposited on SiN during an HFC plasma etching process by forming volatile hydrocarbon species. In the present study, we examine to what extent hydrogen promotes the formation of volatile species containing Si and/or N, which would directly increase sputtering yields of SiN. Our beam experiments have indicated that, under carbon deposition conditions (with 1keV CF^+ ion incidence), the hydrogen content in a SiN film has little effect on the deposition rate of a carbon rich film on SiN. In other words, hydrogen typically contained in the bulk of SiN is not sufficient (probably in quantity) to promote the formation of volatile species on the surface under such conditions to the extent that the deposition rate could be reduced. However, our MD simulation results have also indicated that, under direct interaction of a SiN substrate with HFC ion beams, Si containing volatile species can be indeed desorbed from the surface. The results suggest that, in the presence of a large amount of hydrogen, hydrogen termination of Si and/or nitrogen bonds in the SiN substrate surface region increases the etching rate of SiN.

5:00pm **PS2-TuA10 Molecular Dynamics Analysis of Si Etching with Cl and Br Beams: Ion Incident Angle and Neutral Radical Flux Dependence***, **N. Nakazaki**, H. Tsuda, Y. Takao, K. Eriguchi, K. Ono*, Kyoto University, Japan

Profile anomalies and surface roughness are critical issues to be resolved in plasma etching of nanometer-scale microelectronic devices, which in turn requires a better understanding of the effects of ion incident energy and angle on surface reaction kinetics. In addition, incident neutral radicals also affect the surface reaction kinetics during plasma etching, and thus the etching characteristics are varied by the neutral-to-ion flux ratio. This paper presents a classical molecular dynamics (MD) simulation of Si etching by energetic Cl^+ and Br^+ ion beams and low-energy neutral Cl and Br radicals, using an improved Stillinger-Weber interatomic potential model for Si/Cl and Si/Br systems. Emphasis is placed on a systematic understanding of plasma-surface interactions of Si/Cl and Si/Br systems, which are widely used in manufacturing microelectronic devices.

In the MD simulation, the substrate has a Si(100) surface, which is a square 32.58 Å on a side and contains 72 Si atoms in a monolayer (ML). The simulation cell initially contains 1440 Si atoms (20 ML) in a depth of 26.0 Å, where Si atoms in the bottom layer are fixed during simulation, while periodical boundaries are imposed in the horizontal direction. Energetic Cl^+ and Br^+ ions are injected toward the substrate surface from randomly selected horizontal locations above the target, and neutral Cl and Br atoms are introduced onto the surface prior to every ion incidence. The neutral-to-ion flux ratio was varied in the range Γ_n/Γ_i = 0–100. The ion incident energy was in the range E_i = 20–300 eV, and the ion incident angle was in the range θ_i = 0–90˚. The kinetic energy of neutral atoms was taken to be 1 eV.

Numerical results indicated that in etching by beam only (Γ_n/Γ_i = 0), the surface reaction kinetics exhibit a characteristic of the ion-enhanced etching at lower ion energies, where the etching yield is maximum at normal incidence (θ_i = 0˚), while a characteristics of the physical sputtering at higher energies, where the yield is maximum at off-normal incidence (θ_i = 60–70˚). Similar inclinations for the ion incident angle were obtained with increasing Γ_n/Γ_i, although the thickness of the surface reaction layer increases a little and the etch yield increases significantly with increasing Γ_n/Γ_i. These imply that impinging ions disarrange the surface Si lattice and weaken the binding force of Si atoms on the top surface, and incident neutral radicals etch surface Si atoms whose binding force with the neighbor Si atoms becomes lower than that of Si atoms in the original diamond lattice. These effects are clearly observed for Si/Br system, as compared to for Si/Cl system.

5:20pm **PS2-TuA11 Controlling Correlations Between Ion and UV/VUV Photon Fluxes in Low Pressure Plasma Materials Processing***, P. Tian, **M.J. Kushner***, University of Michigan

The importance UV and VUV photon fluxes during plasma materials processing has been recognized through the damage these fluxes may cause in devices being fabricated and in adversely affecting the permittivity of low-k dielectrics such as SiOCH through demethylation. Recently, synergistic effects between ions and photons have been observed in the roughening of photoresist [1] and in sub-threshold etching of silicon in Cl containing gas mixtures.[2] The growing awareness of the importance of UV and VUV photon fluxes in low pressure plasma materials processing, and the possibility of there being synergies with ion fluxes, motivates development of methods to separately optimize UV/VUV and ion fluxes. For example, one may wish to maximize or minimize the overlap in time between the UV/VUV and ion fluxes depending on the particular process. In this talk, we report on results from a computational investigation of low pressure inductively and capacitively coupled plasmas with the goal of determining the degree to which UV/VUV and ion fluxes can be separately controlled. The model used in this investigation is a 2-dimensional plasma hydrodynamics model with radiation transport. Two strategies are being investigated. The first is pulsed plasmas which rely on the different time scales for production and transport of photons and ions to the substrate during the pulsed period to provide for some degree of separate control of the fluxes. The second is semi-remote plasma sources which rely on isolation of the photon sources and transport of ions to control the ratio of photon and ion fluxes to the substrate.

[1] T-Y. Chug, et al., Plasma Proc. Polymer **8**, 1068 (2011)

[2] H. Shin et al., J. Vac. Sci. Technol A **30**, 021306 (2012)

* Work supported by the Semiconductor Research Corp. and DOE Office of Fusion Energy Sciences

5:40pm **PS2-TuA12 Formation Mechanisms of Nanoscale Surface Roughness and Rippling during Plasma Etching and Sputtering of Si under Oblique Ion Incidence***, **H. Tsuda**, Y. Takao, K. Eriguchi, K. Ono*, Kyoto University, Japan

Three-dimensional measurement and prediction of atomic-scale surface roughness on etched features become increasingly important for the analysis of line edge roughness (LER) and line width roughness (LWR) on feature sidewalls; however, the feature profiles are too small and/or too complex to measure the surface roughness on bottom surfaces and sidewalls of the etched features. To predict the surface roughness on atomic/nanometer scale, we have developed our own three-dimensional atomic-scale cellular model (ASCeM-3D) [1] and feature profile simulation. In this study, emphasis is placed on a better understanding of the formation mechanisms of nanoscale surface roughening and rippling during Si etching and sputtering under oblique ion incidence.

In the ASCeM-3D model, the simulation domain is divided into a number of small cubic cells of $L = \rho$Si-1/3 = 2.7 Å, where ρSi = 5.0 x 1022 cm−3 is the atomic density of Si substrates. Ions and neutrals are injected from the top of the simulation domain, and etch and/or sputter products are taken to be desorbed from etching surfaces into microstructural features, where two-body elastic collision processes between incident ions and substrate atoms are also taken into account to analyze ion reflection on etched feature surfaces and penetration into substrates. The ASCeM-3D takes into account surface chemistries based on the Monte Carlo (MC) algorithm [2-4],

including adsorption and reemission of neutrals, chemical etching, ion-enhanced etching, physical sputtering, and redeposition of etch and/or sputter products on feature surfaces. The etch yield of ion-enhanced etching and sputtering depending on ion incident energy and angle is taken from the empirical models.

Numerical results indicated that the ripple structures occur on etched surfaces, depending on incident angle of ions. The surfaces are randomly roughened in the case of Cl2 plasma etching for an ion incident angle θi = 0° or normal incidence of ions. For increased θi = 45°, the ripples are formed perpendicular to the direction of ion incidence, while parallel to that of ion incidence for further increased θi = 75°. These imply that the angular dependence of energy transfer processes from an incident ion to substrate atoms largely affects the evolution of feature profiles and surface roughness on atomic/nanometer scale.

[1] H. Tsuda *et al*., Jpn. J. Appl. Phys. **50** (2011) 08JE06.

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

[3] H. Tsuda *et al*., Thin Solid Films **518** (2010) 3475.

[4] H. Tsuda *et al*., Jpn. J. Appl. Phys. **49** (2010) 08JE01.

Advanced Surface Engineering
Room: 22 - Session SE+PS-TuA

Atmospheric Pressure Plasmas
Moderator: H. Barankova, Uppsala University, Sweden, P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:00pm **SE+PS-TuA1 Plasma Medicine: The Journey of a New Field of Research, from Killing of Bacteria to Killing of Cancer Cells**, ***M. Laroussi***, Old Dominion University **INVITED**

Research on the biomedical applications of low temperature plasmas started with few limited experiments mainly concerned with the ability of plasma to kill harmful microorganisms, especially bacteria as it relates to sterilization of abiotic and/or biotic surfaces (such as tissues). Low temperature plasmas produce a potent cocktail of highly reactive chemical species including reactive oxygen species (ROS) such as O, O_2^-, and OH and reactive nitrogen species (RNS) such as NO and NO_2. These species are known to exhibit strong oxidative properties and can trigger signaling pathways in biological cells. For example oxidation of the lipids and proteins that constitute the membrane of biological cells leads to the loss of their functions. In such environment bacterial cells were found to die in minutes or even seconds, depending on the strain. Plasmas were also found to be an effective method to control the proliferation of biofilms. Biofilms are very resistant to chemicals found in detergents and even to antibiotics. Therefore, if not controlled, biofilms (including dental plaque, for example) could represent serious health hazards.

Experiments on eukaryotic cells demonstrated that under some conditions, low temperature plasmas appear to cause little damage to living animal and plant tissues. For example, skin fibroblast cells are found to remain viable under plasma conditions that can be lethal to bacterial cells. The proliferation of fibroblasts is an important step in the wound healing process. The ability of plasma to kill bacteria and to accelerate the proliferation of specific tissue cells opened up the possibility to use plasma for the healing of chronic wounds such as diabetic ulcers. Tens of thousands of amputations occur every year in the US alone because of the inability of present medical methods to heal chronic wounds.

Low temperature plasmas have been found to be able to trigger apoptosis in cancer cells. Apoptosis is a natural process of “programmed” cell death. Cancerous cells lose the ability to initiate such a killing process. However, mediated through its specific chemical species, plasmas can trigger the signaling pathway that can start the cascade of events that result in apoptosis. This unique plasma capability opened up the possibility to use plasma for cancer treatment.

Low temperature plasmas therefore constitute a new transformational approach to healthcare referred to as Plasma Medicine [1]. In this paper background work as well as new results both in fundamental understanding and applications will be discussed.

References

[1] M. Laroussi, “Low Temperature Plasmas for Medicine?”, *IEEE Trans. Plasma Sci.***37**, 714 (2009).

2:40pm **SE+PS-TuA3 VHF Atmospheric Glow Discharge: Electrical and Optical Characterization for Multiple Gases**, ***B. Byrns***, *A. Lindsay, S. Shannon, A. McWilliams, S. Hudak, J. Cuomo*, North Carolina State University

Atmospheric plasmas have the potential to increase the efficiency of many processes involving interactions between materials and plasma due to the increased reactive species densities in the plasma. One challenge in the integration of these sources into high volume applications is the difficulty of producing large area, high density atmospheric plasmas without reaching thermal equilibrium or relying on the formation of arcs; a secondary challenge is the formation of these discharges without helium or other rare gas species that are typically used to sustain atmospheric glows. In this work a large area atmospheric pressure glow discharge operating at 162MHz has been created utilizing a VHF ballasting effect [1]. An electrical model paired with a simple global plasma model is used to characterize the electrical properties of the plasma. Several different feed gases including air, CO2, nitrogen, and argon are used to validate the model and study the production of reactive species in the plasma volume; both of these endeavors also enable intelligent process setpoint design to achieve the necessary operating conditions for various gases. These measurements are made using various electrical and optical diagnostics including OES, B-loop probe measurements, and in-line RF metrology. The effects of increasing the pressure, through the use of nozzles, are examined and used to further refine and validate the system model. This greater understanding of the plasma allows for the potential to increase the size of the plasma, allowing for an increase in the number of reactive species and thus an increase in the efficiency for the treatment of surfaces. Currently the plasma is being studied for use in the removal of HDPE from surfaces as well as for the treatment of water. Preliminary results for both of these applications will be presented.

[1] Brandon Byrns et al 2012 J. Phys. D: Appl. Phys. 45 195204

* Work supported by the State of North Carolina, SERDP contract 1762, and by a generous gift donation from Advanced Energy Incorporated, Verity Instruments, and Bird Technologies.

3:00pm **SE+PS-TuA4 Atmospheric Pressure Glow Discharge for Point-of-Use Water Treatment**, ***A. Lindsay***, *B. Byrns, S. Shannon, D. Knappe*, North Carolina State University

Treatment of biological and chemical contaminants is an area of growing global interest where atmospheric pressure plasmas can make a significant contribution. Atmospheric plasmas have demonstrated the potential to reform aqueous chemistry[1] and mitigate water contamination[2]. One of the key challenges is scaling of these systems for volume processing. A large volume VHF coaxial plasma source has been developed that enables scale up of these systems under ambient air conditions, addressing volume processing and operating cost due to the absence of a noble gas carrier to sustain a volume glow.[3] The 162 MHz atmospheric glow discharge presented here offers several features uniquely applicable for disinfection. Because of ballasting effects, attributable to the very high drive frequency, the electric discharge is maintained at a steady glow, allowing formation of critical non-equilibrium chemistry. High densities, $n_e = 10^{11}$-10^{12},have been recorded. The atmospheric nature of the device permits straightforward and efficient treatment of material samples. Using air as a process gas, $[H^+]$ concentrations in 150 milliliter tap water samples have been shown to drop five orders of magnitude after five minutes of discharge exposure. Recent literature has demonstrated that increasing acidity is strongly correlated with a solution’s ability to deactivate microbial contaminants.[1] The work presented here will explore the impact of treatment gas, system configuration, and power density on water treatment including disinfection and PFC abatement. An array of plasma diagnostics including optical emission spectroscopy and electrical measurement of plasma discharge condition are combined with post-process water chemistry analysis including Quanti-Tray analysis of coliform and E.coli bacteria, gas chromatography, and mass spectrometry. Continued development of volume processing atmospheric plasma disinfection technology offers promise for point-of-use treatments in developing areas of the world, potentially supplementing or replacing supply-dependent chemical and weather-dependent solar disinfection methods.

1. Traylor (2011) J. Phys. D: Appl. Phys. 44 (2011) 472001

2. Takeuchi (2011) IEEE Trans. On Plasma Sci. 39(12) 3358-3363

3. Byrns (2012) J. Phys. D: Appl. Phys. 45 (2012) 195204

* Work supported by generous gift donations from Bird Technologies, Advanced Energy, and Verity Instruments

4:00pm **SE+PS-TuA7 Cold Atmospheric Plasma in Liquids**, ***H. Barankova***, *L. Bardos*, Uppsala University, Sweden

Atmospheric pressure plasmas and their applications, especially those based on non-thermal processes, have been extensively studied in the last decade,

with focus on surface treatment, coatings and gas conversion. Individual applications depend on the current status of development in atmospheric pressure plasma sources. The plasma source based on the Fused Hollow Cathode (FHC) geometry was developed for generation of plasma in liquids. Effect of various generation regimes on the performance of plasma and on plasma distribution in water is studied without and with different auxiliary gases. The paper also discusses importance of the plasma source/reactor design for control of plasma chemical kinetics and comments on advantages and limitations of atmospheric plasma.

Acknowledgements: this work is part of the GREENCOAT project, financed by the Brussels Region, and by the IAP project "physical chemistry of plasma surface interactions", funded by the Federal Government, Belgium.

4:20pm **SE+PS-TuA8 Characterization of Amorphous and Microcrystalline Si Films Grown in Atmospheric-Pressure Very High-Frequency Plasma**, ***H. Kakiuchi***, *H. Ohmi, T. Yamada, A. Hirano, T. Tsushima, K. Yasutake*, Osaka University, Japan

Hydrogenated amorphous silicon (*a*-Si) and microcrystalline silicon (*μc*-Si) prepared at low temperatures are promising thin film materials for use in large-area electronic devices. The goal of our study is to develop a highly efficient deposition process of good-quality *a*-Si and *μc*-Si films on polymer substrates using an atmospheric- pressure (AP) plasma technology in which stable reactive plasma excited by a 150-MHz very high-frequency (VHF) power under AP is effectively used.

The experiments were conducted in an AP plasma CVD system that had a parallel-plate-type electrode (2x8 cm^2), whose surface was coated by alumina of ~0.1 mm thickness. By supplying a VHF power through an impedance matching unit, AP $He/H_2/SiH_4$ plasma was stably confined in the narrow gap region (0.3–0.7 mm) between the electrode and a substrate. Under a constant process pressure of $1x10^5$ Pa, VHF power density (P_{VHF}), H_2 and SiH_4 flow rates, plasma gap and substrate heating temperature (T_{sub}) were varied as principal parameters. Si dusty particles formed by gas-phase condensation in the outside of the plasma region were completely removed by sucking the gas flow before their adhering to the substrate surface.

By examining the influence of gas residence time in the plasma on the film growth behavior, it was shown that the source SiH_4 gas was immediately decomposed after being introduced into the plasma region and contributed to the film growth. Under the condition of P_{VHF} = 14 W/cm^2, H_2 and SiH_4 flow rates of 500 and 50 SCCM, respectively (H_2/SiH_4 = 10), and T_{sub} = 220 °C, the film started to crystallize in only 0.3 msec. Both increasing P_{VHF} and H_2/SiH_4 ratio caused the decrease in gas residence time necessary for the phase transition of the resultant Si films. On the other hand, an excessively long gas residence time (> 1 msec) led to the formation of highly crystallized *μc*-Si films even if H_2 was not added to the process gas mixture. However, such *μc*-Si films showed poor electrical properties, which resulted from the sparse film structure without enough passivation of the grain boundaries with amorphous Si tissues. These suggest that the precise control of gas residence time is primarily important for the formation of good-quality *a*-Si and *μc*-Si films using AP-VHF plasma, together with the optimization of P_{VHF} and H_2/SiH_4 ratio.

The *a*-Si and *μc*-Si films deposited with high rates (>10 nm/s) in AP $He/H_2/SiH_4$ plasma were used as the channel layers of bottom-gate thin film transistors (TFTs). The performance of the TFTs will be presented in the conference.

4:40pm **SE+PS-TuA9 Atmospheric Plasma Polymerization of Esters: Tuning the Coating Chemistry by Tuning the Precursor Chemistry**, *B. Nisol, A. Batan,* Université Libre de Bruxelles, Belgium, *A. Kakaroglou, M. Wadikar, G. Scheltjens, G. Van Assche, B. Van Mele, I. De Graeve, H. Terryn,* Vrije Universiteit Brussel, Belgium, ***F. Reniers***, Université Libre de Bruxelles, Belgium

The influence of the chemical environment of an ester function on the plasma polymerization process and on the chemical structure of the deposited coating is investigated, and the consequences on the coatings properties (barrier and adhesion) are discussed. Allyl methacrylate (AMA), n-propyl methacrylate (nPMA) and propyl isobutyrate (PIB) containing respectively two, one and no double bonds were injected in a home made dielectric barrier discharge reactor. Argon was used as the main plasma gas, and the power of the discharge was varied from 30 to 80 W. The thickness of the deposited coating was determined by visible spectroscopic ellipsometry and allowed to calculate the deposition rate. The surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS) and the bulk structure was analyzed by reflection – absorption infrared spectrometry (IRRAS). Differential scanning calorimetry was used to probe the remaining unreacted groups in the coating. The results evidence a great change in the polymerization rate that depends on the presence of the double bonds. Moreover, the concentration of ester groups at the surface of the coatings also depends on the surrounding double bonds present in the precursor. Indeed, whereas the relative amount of ester groups in poly-AMA remains stable when increasing the plasma power, it drops drastically for poly-PIB. A stabilization of the ester groups by the double bonds is suggested.

Wednesday Morning, October 31, 2012

Energy Frontiers Focus Topic
Room: 15 - Session EN+PS-WeM

Plasmas for Photovoltaics and Energy Applications
Moderator: J.-P. Booth, LPP-CNRS, Ecole Polytechnique, France

8:00am **EN+PS-WeM1 Electron Driven C_1-chemistry: Direct Conversion of Methane to Synthetic Fuels**, ***T. Nozaki***, Tokyo Institute of Technology, Japan **INVITED**

Currently, industrial material and energy conversion technology platform consists of thermochemical processes including various catalytic reactions. Existing industry scale technology and related science has already been well established; nevertheless, further improvement in energy efficiency and material saving are demanded. Drastic reduction of CO_2 emission is also drawing keen attention with growing concern of energy and environmental issues. Green chemistry is a rapidly growing field of science and technology, and often highlights renewable bioenergy, bioprocesses, solar photocatalysis of water splitting, and CO_2 regeneration as synthetic fuels. Plasma catalysis of hydrocarbon feedstock is also highlighted as an important part of the innovative next generation green technologies that meet the need for energy saving, environment protection, and material preservation [1-4]. Non-thermal plasma uniquely generates reactive species independently of reaction temperature, and these species are used to initiate chemical reactions at unexpectedly lower temperatures than normal thermochemical reactions. Non-thermal plasma thus broadens the operation window of existing chemical conversion processes, and ultimately allows modification of the process parameters to minimize energy and material consumption. We specifically focus on dielectric barrier discharge (DBD) as one of the viable non-thermal plasma sources for practical fuel reforming. In the presentation, room-temperature one-step conversion of methane to synthetic fuels such as methanol, hydrogen, and syngas (H_2+CO) using a microplasma reactor is highlighted. Not only practical background of the project, but also unique characteristics of plasma fuel reforming such as non-equilibrium product distribution is presented [5-7].

1. T Nozaki et al: *Journal of the Japan Petroleum Institute*, **54**(3) (2011) 146.

2. The special issues on " Non-thermal Plasma Assisted Fuel Conversion for Green Chemistry ", *J Phys D: Appl Phys.*, **44**(23), 2011

3. A Gutsol: Handbook of Combustion, Vol.5 New Technology, Wiley-VCH, 323 (2010)

4. H L Chen et al: *Appl. Catal. B: Environmental*, **85** (2008) 1.

5. T Nozaki et al: *Chemical Engineering Journal*, **166** (2011) 288– 293.

6. T Nozaki et al: *Energy & Fuels*, **22** (2008) 3600–3604.

7. T Nozaki et al: *Pure and Applied Chemistry,***78**(6) (2006) 1147–1162.

8:40am **EN+PS-WeM3 Plasma-assisted CO_2 Conversion as Candidate Element in Future Solar Fuel Economy**, *S. Welzel, S. Ponduri, F. Brehmer, M. Ma, M.C.M. van de Sanden,* ***R. Engeln***, Eindhoven University of Technology, the Netherlands

Recently research in 'solar fuels' has been stimulated by the forthcoming depletion of fossil fuels along with a slowly increasing share of intermittently available renewable sources. New efficient methods of harvesting renewable (e.g. solar) energy and its storage in high energy density chemical fuels are therefore highly desirable. CO_2 and its recycling into 'solar fuels' will be an essential element in the future transport and energy infrastructure. Plasma-processing of CO_2 in the gas phase under low-temperature non-equilibrium conditions is thereby a promising alternative to specifically tackle the rate-limiting dissociation into CO. Two aspects of such a plasma-assisted CO_2 treatment have been studied and are detailed in this contribution.

Firstly, the direct hydrogenation of CO_x in a plasma-expansion created from mixtures of Ar and H_2 was investigated. Different (metallic) surface materials were employed to assess the influence of surface reactions on the molecule formation. Mass-spectrometry and infrared absorption spectroscopy were applied to quantify the gas phase composition of such argon-ion and hydrogen-radical enhanced plasmas. Although CO was a main product with up to 50 % conversion yield, the separation of CO_2 dissociation and subsequent hydrogenation was strongly suggested to optimise both processes individually. Furthermore it transpired that plasma-catalysis require new surface materials that are different from conventional catalysts: a copper surface typically reduced the CO and CH_4 yields by 50 %.

Secondly, to particularly account for the individual optimisation of the CO_2 dissociation and scrutinise the (energy) efficiency of the conversion process dielectric barrier discharges in CO_2 were studied. The focus was on establishing a consistent energy-balance of the proposed plasma-assisted route and involved the analysis of energy injected to the power supply, the transfer to the discharge and the correlation with the CO_2 conversion. Through reduction of loss channels in the resonance circuit operated in the kHz-range clearly more than 50 % of the input power were directly injected to the plasma. Plasma parameters such as electron and vibrational temperatures and the population distribution of excited species were determined to further characterise the excitation and dissociation channels in the CO_2 plasma.

9:00am **EN+PS-WeM4 Novel Processing Routes of Silicon Nanocrystals in a Remote Expanding Thermal Plasma for Photovoltaic Applications**, ***I. Dogan****, Eindhoven University of Technology, Netherlands, *S.L. Weeks,* Colorado School of Mines, *K. Dohnalova, T. Gregorkiewicz,* University of Amsterdam, Netherlands, *S. Agarwal,* Colorado School of Mines, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research, Netherlands

The interest in silicon nanocrystals (Si-NCs) has considerably increased since the observation of carrier multiplication and separation between adjacent Si-NCs. This mechanism might potentially enable a more efficient solar spectrum conversion. For successful integration of Si-NCs into solar cells, the key issues are size control, crystalline quality, surface preparation and cost efficient production of Si-NCs. Previous works have failed to address the latter point because they require multiple production steps yet with an insufficient amount of produced Si-NCs. Here, a novel synthesis method of Si-NCs by using a remote expanding thermal plasma (ETP) is presented, that allows a direct utilization for large scale production. One-step route synthesis of Si-NCs is realized in an argon/silane plasma with remarkable throughputs above 100mg/min of Si-NCs. Formation of Si-NCs is favoured by means of silane polymerization reactions. In contrast to the common belief of particle coagulation, all Si-NCs are found to be formed by nucleation as revealed from TEM analysis of the Si-NCs produced. TEM, Raman spectroscopy (RS) and photoluminescence spectroscopy (PL) consistently demonstrate that the Si-NCs have a size distribution in the range 2-140nm which is related to differences in residence times in the different zones of the reactor. To move towards a better control of the size distribution, a series of size separation experiments is discussed. Two approaches are proposed: spatial confinement of the plasma zones where the smaller Si-NCs are formed or a time modulation of the silane flow injected into the reactor. It will be shown that using these methods an average Si-NC size distribution of 5nm can be reached. Moreover, based on the results of time modulation, the role of different plasma species on the formation of small and large Si-NCs will be discussed. The observation of step-like enhancement of luminescence quantum yield with increased photon energy, which is a sign of carrier multiplication between Si-NCs will be discussed. It is expected that the ETP approach is capable to dramatically increase the production efficiency of Si-NCs to scalable throughputs without any loss of quality.

9:20am **EN+PS-WeM5 Growth of Microcrystalline Silicon using Tailored Voltage Waveform Driven Plasma Processes: From Materials to PV Devices**, ***E.V. Johnson***, LPICM-CNRS, Ecole Polytechnique, France, *S. Pouliquen, P.A. Delattre, J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France **INVITED**

The use of non-sinusoidal, radio-frequency (RF) « tailored » voltage waveforms (TVW's) to drive plasma processes in a capacitively coupled plasma reactor allows one to decouple the injected power from the mean ion bombardment energy (IBE) at the substrate. Also known as the Electrical Asymmetry Effect (EAE), this decoupling stems from a controllable division of the sheath voltage between the two electrodes when an asymmetric voltage waveform is applied to one of the electrodes. In a symmetric reactor, this effect manifests itself through the presence of a self-bias voltage (V_{DC}), and as dramatic changes in this parameter in an asymmetric one. For example, the application of a "peaks" waveform to the RF electrode - consisting sharp pulses separated by plateaus - results in a large, negative V_{DC}, and thus a reduction in the IBE at a substrate on the grounded electrode. A "valleys" waveform results in the opposite, while both waveforms inject the same power into the plasma.

Such independent control over the sheath voltages is very useful when applied to the deposition by PECVD of thin-films of materials needing a high radical flux but low IBE, such as hydrogenated microcrystalline silicon

* Coburn & Winters Student Award Finalist

(μc-Si:H). By controlling the growth conditions of the μc-Si:H thin films through the shape of the waveform, one can control many aspects of the film properties (Raman crystallinity, density, hydrogen bonding, surface morphology, and electronic properties) without changing any other process conditions. In particular, the optical response of the films (and film surfaces) can be observed in-situ during growth using spectroscopic ellipsometry, thus linking the redistribution of the sheath voltages to the growth dynamics. Furthermore, we show that when TVW's are used to decrease the IBE during the growth of the absorber layer of thin-film solar cells, good device properties at acceptable deposition rates are obtained.

A promising aspect of this technique is the prospect of achieving process control without modifying the core of an existing reactor chamber. However, the counteracting challenge is that of efficiently coupling multiple harmonics to the reactor simultaneously, and these two facets will also be discussed.

10:40am **EN+PS-WeM9 Measurement and Control of Ion Energies in Dual Frequency Capacitive Hydrogen Discharges**, ***E. Schuengel****, S. Mohr, J. Schulze, U. Czarnetzki*, Ruhr-University Bochum, Germany

In plasma processing applications, capacitively coupled radio frequency (CCRF) discharges are widely used. A typical example is the manufacturing of silicon thin film solar cells using PECVD in a geometrically almost symmetric capacitive parallel plate discharge. For these applications, one of the major aims is the control of the fluxes and properties of radicals and ions at the substrate surface, thus controlling the surface chemistry and optimizing the (electrical) properties of the deposited film and/or the deposition rate. In particular, the shape of the ion velocity distribution function (IVDF) plays a crucial role [1]. The IVDF can be controlled to some extent in CCRF discharges driven by two substantially different frequencies, where the low frequency component is used to modify the ion energy while the total ion flux should be adjusted via the high frequency component. However, recent investigations have shown that this method is limited to a rather narrow window of discharge operating conditions [2]. As opposed to this concept, the Electrical Asymmetry Effect (EAE) uses the excitation via two consecutive harmonics to generate an asymmetric discharge even in geometrically symmetric discharge configurations [3]. Here, the symmetry of the discharge, the DC self bias, and the ion energy at the electrode surfaces are controlled via the phase angle between the two frequencies. In this study, the EAE is investigated in a discharge setup, which is similar to the ones described in the above example. A combination of 13.56 MHz and 27.12 MHz is applied to one electrode. The discharge is ignited in pure hydrogen at pressures of several hundred Pascals. Under these conditions, H3+ ions are the dominant ion species. A plasma process monitor is implemented into the center of the grounded electrode, allowing to measure the H3+ IVDF. The results show that the mean ion energy changes as a function of the phase angle, while the ion flux is kept almost constant. However, the control range of the ion energy via the EAE is limited and the shape of the IVDF shows a dependence on the phase angle. These experimental findings are understood in the frame of a simple model.

Funding by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (0325210B) is gratefully acknowledged.

[1] S. Nunomura and M. Kondo 2008 Appl. Phys. Lett. **93** 231502

[2] J. Schulze et al. 2009 Plasma Sources Sci. Technol. **18** 034011

[3] U. Czarnetzki et al. 2011 Plasma Sources Sci. Technol. **20** 024010

11:00am **EN+PS-WeM10 Raman Study of the Properties of Free Standing Silicon Nanocrystals Using Laser Induced Thermal Heating**, ***L. Han****, A.H.M. Smets, M. Zeman*, Delft University of Technology, Netherlands

Nanocrystals (NCs) exhibit unique physical properties which might open routes to new photovoltaic concepts conquering the Shockley-Queisser limit of single junction solar cell devices, such as multiple-exciton-generation (MEG) and down conversion using space-separated-quantum-cutting (SSQC). In addition, the strong dependence of the band gap of NCs on their sizes, allows the design of novel multi-junction solar cells. For these reasons, NCs made of variety of direct and indirect semiconductor materials, have been extensively studied in recent years. In this contribution we focus on silicon, the most dominant material in PV technology. Challenges in the processing of Si NCs are controlling their size distribution and passivation of surfaces to prevent unwanted Shockley-Read-Hall recombination of generated charge carriers.

The Si NCs studied in this paper are synthesized using the expanding thermal plasma chemical vapor deposition (ETP-CVD) technique with the advantage of incredible high yield, deposition rate, room temperature fabrication, low cost, high purity and post-surface passivation treatment based on plasma processing. Using the ETP-CVD technique free standing Si NCs with a wide variety of properties have been processed. The dependence of the processing conditions are studied using high resolution transmission electron microscopy. Furthermore, the surface oxidation kinetics of free standing Si NCs without any post-deposition surface-passivation-treatment is studied using IR absorption spectroscopy.

The main focus in this contribution is an unconventional Raman spectroscopy analysis on the free standing Si NCs. In this approach, Si NCs are additionally heated using a laser probe to study the quantum confinement effects of the Si NCs in more detail. An interesting huge red Raman peak shift for the transverse optic mode (520 cm-1) of around 30 cm-1 and a width enhancement of 19.1 cm-1 are observed with the increasing power of the probe laser. We argue that the shift is due to the laser induced thermal heating of the Si NCs in line with analysis based on the ratio of the Anti-Stokes-to-Stokes peak of the free standing Si NCs [1]. As a reference, the Raman spectra of amorphous silicon and microcrystalline silicon thin films are studied using the same approach. This experiment shows that thermal conduction between the free standing Si NCs is inefficient in contrast to the Si films, which allows the Si NCs to be heated up by laser light more efficiently.

[1] Khriachtchev et al., JAP 100, 053502 (2006)

11:20am **EN+PS-WeM11 Fabrication of 3D Array Si Quantum Dots Superlattice using Biotemplate and Neutral Beam Etching**, ***M.E. Fauzi****, M. Igarashi, W. Hu, S. Samukawa*, Tohoku University, Japan

Quantum dots have been used in many novel optoelectronic devices due to its quantum effect characteristics. To further improve quantum dots light absorption efficiency, it is vital to increase number of quantum dots while keeping straight alignment in vertical direction. However, in the conventional method using bottom-up approach, fabricated quantum dots structure is not uniform and well-aligned in vertical direction, while the conventional top-down etching has limitations in fabrication of nanometer size and leaves high-density defects. In previous study, we have fabricated well-ordered arrangement of high-density 2 dimensional (2D) array (7×10^{11} cm^{-2}) silicon nanodisk (Si-NDs) with a new process using bio-template and damage-free neutral beam etching (NBE). In this paper, we developed technology for fabricating 3D array of Si NDs with single step NBE technique and biotemplate technology, focusing on well-aligned structure in vertical direction.

Firstly, we deposited 4 layers of 4 nm-thick Si layer with 2 nm-thick silicon carbide (SiC) as its matrix using thin film deposition technique. Then, bio-template was quasi-hexagonally arranged and used as mask during our etching process.These bio-templates provide 6 nm space between etching masks. After NBE process, high aspect ratio of 12 is achieved. The key technology in our approach is to utilize low-selectivity etching process to etch high aspect ratio structure in single step. Single step etching is made possible for three reasons. First, oxide layer on top of our Si/SiC structure was first removed by NF_3 gas/hydrogen radical treatment. Secondly, SiC that was used as matrix material has a comparable etching rate compare to Si. In our research, we make use of Si/SiC's low selectivity (1.3) to conduct a well-aligned vertical etching process. Thirdly, a high selectivity for Si/SiC structure to iron-core etching mask. After chlorine NBE process, iron-core mask pattern was precisely transferred, and anisotropic etching profile was achieved. Our SEM images of the top-view and cross-section view exhibits well-aligned, uniformity, high aspect ratio nano-columns. Lastly, we deposit SiC layer to complete Si/SiC matrix. As a result, we successfully fabricated 4 layers-stacked Si-NDs with sub-10 nm in diameter and 2 nm space between nanodisks.

We hope quantum dots superlattice fabricated by our technology could be used in quantum dot solar cell application for higher conversion efficiency.

11:40am **EN+PS-WeM12 Two-dimensional Simulations of Hydrogen and Hydrogen/Silane Capacitively Coupled Dual Frequency Discharges**, ***S. Mohr****, E. Schuengel, J. Schulze, U. Czarnetzki*, Ruhr University Bochum, Germany

Capacitively coupled radio-frequency (CCRF) discharges are commonly used in surface processing applications, for example the deposition of thin films. One of the most important challenges in optimizing CCRF discharges for this usage is achieving the ample and independent control of flux and energy of ions and reactive species at the surfaces, as these properties determine the quality and deposition rate of the films. This independent control can be attained by using electrically asymmetric discharges which use two consecutive harmonics to excite the plasma; the ion energy can be controlled by the phase between the two frequencies while the flux stays constant. The feasibility of this method has been demonstrated by both experiments and simulations in various gas mixtures [1-3], although limitations have been observed, for example in highly electronegative discharges.

Hydrogen is part of many gas mixtures used in industrial applications such as hydrogen/silane mixtures in the production of solar cells. Two traits, which distinguish hydrogen discharges from the already investigated gas mixtures, are the high ion mobility and the regular occurrence of field reversals during the sheath collapse. Additionally, deposition processes are usually carried out at quite high pressures of several 100 Pa. We conduct two-dimensional simulations of such discharges covering a wide range of discharge conditions (pressure: 20 Pa – 500 Pa, pure hydrogen discharges and hydrogen/silane mixtures) using the simulation tool Hybrid Plasma Equipment Model (HPEM) by Mark Kushner [4]. The focus of our investigations lies on the influence of high pressures, field reversals, and high ion mobilities on the separate control of ion energy and ion flux. For example, we observe a significant reduction of the ion energy control range, if field reversals are the main ionization source of the discharge. The physical mechanisms behind this effect and others occurring in hydrogen and hydrogen/silane - discharges will be discussed.

Funded by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (0325210B).

[1] U. Czarnetzki et al. 2011 *PSST***20** 024010

[2] E. Schüngel et al. 2011 *J. Phys. D.***44** 285205

[3] J. Schulze et al. 2011 *PSST***20** 045008

[4] M. Kushner 2009 *J. Phys. D***42** 194013

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+AS+BI+PS+SS-WeM

Graphene Surface Chemistry, Functionalization, Biological and Sensor Applications
Moderator: D.K. Gaskill, U.S. Naval Research Laboratory

8:00am **GR+AS+BI+PS+SS-WeM1 Structural Analysis of Chemically Functionalized Epitaxial Graphene with High-Resolution X-ray Reflectivity**, *J.D. Emery, Q.H. Wang, M. Zarrouati,* Northwestern University*, P. Fenter,* Argonne National Laboratory*, M.C. Hersam,* ***M.J. Bedzyk***, Northwestern University

For graphene to realize its potential in next-generation electronics it must be incorporated with a variety of materials to form devices. Recently, the use of self-assembled organic monolayers deposited on epitaxial graphene (prepared by graphitization of the 6H-SiC(0001) surface) has been effective in the functionalization of the bare graphene sheet, enabling the additional chemistry necessary for device fabrication. In this work, we present high-resolution X-ray Reflectivity (XRR) studies of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on epitaxial graphene. Initially, a model-independent vertical electron density profile of the graphene/silicon carbide interface is retrieved with the use of Feinup-based error correction algorithms in order to minimize ambiguities that can arise from model-based methods. This retrieved structure is then used as the foundation for model-based analysis, from which the final structures are extracted. A series of structures comprising 0, 1, and 2MLs of PTCDA deposited on 1-2ML graphene are discussed. The interlayer spacing between the PTCDA and top graphene layer are revealed to be approximately 0.35 nm, which supports the view that the PTCDA molecules are interacting only weakly (van der Waals) with the graphene layer. In addition to the characterization of PTCDA-functionalized graphene, we will also demonstrate the efficacy of these molecules to form a weakly-interacting seeding layer for subsequent growth of high-k dielectrics via atomic layer deposition.

8:20am **GR+AS+BI+PS+SS-WeM2** ***In Situ*** **FT-IR Study of Graphene Fluorination using** $\mathbf{XeF_2}$, ***J.-F. Veyan***, *N. Shafiq,* University of Texas at Dallas*, K. Novoselov,* University of Manchester, UK*, Y.J. Chabal*, University of Texas at Dallas

Graphene fluorination to obtain fluorographene has been successfully realized by exposing graphene flakes to molecular Xenon-Difluroride [1-3]. To gain a mechanistic understanding of XeF_2 reaction with the graphene flakes, an all-aluminum custom-made two-stage reaction cell has been designed to fit into the main sample compartment of an FTIR Nicolet 6700 interferometer, for *in situ* infrared absorption spectroscopy. The first stage is a clean expansion chamber to isolate the pure XeF_2 in its gas phase, from solid XeF_2 (powder) stored in a storage vessel. The XeF_2 vapor is extracted by opening the valve V1 to the storage chamber and its pressure (up to ~4 Torr) is controlled by the valve V2. The second stage is a reactor equipped with two KBr windows, allowing the IR beam to penetrate and exit the enclosure. A pneumatic valve allows the transfer of gaseous XeF_2 from stage 1 into stage 2. Pressures in both storage and reactor chambers are measured with Baratron gauges (Ga1, Ga2). To avoid any contamination of the reactor and sample holders during sample preparation and loading, a N_2-purged glove bag is placed over the reactor to maintain a controlled environment. The graphene flakes in suspension in a NMP (N-Methylpyrrolidon) solution, are transferred onto three mechanically polished Aluminum plates at a temperature of 70°C. The plates are then mounted on the specially designed 3-reflection sample holder flange designed to fit stage 2.

By varying the sample temperature from 20 to 200°C as well as the XeF2 pressure in the reactor stage from 0.1 to 4 Torr, the chemical attachment of fluorine on graphene is identified from a comprehensive FT-IR study performed under under industrial conditions. Fluorine attached out of plane can be easily differentiated from fluorine attached at edges (i.e. remaining within the basal plane) and terminating the edge atoms.

[1] R. R. Nair, et al., Small **6**, 2877 (2010).

[2] J. T. Robinson, et al., Nano Letters **10**, 3001 (2010).

[3] K.-J. Jeon, et al., Acs Nano **5**, 1042 (2011).

8:40am **GR+AS+BI+PS+SS-WeM3 Molecularly Resolved Chemical Functionalization of Graphene**, ***M.C. Hersam***, Northwestern University **INVITED**

Graphene has emerged as one of the leading materials in condensed matter physics due to its superlative electrical and mechanical properties. With an eye towards expanding its functionality and applications, this talk will highlight our latest efforts to tailor the surface chemistry of graphene [1]. At the molecular scale, we employ ultra-high vacuum (UHV) scanning tunneling microscopy (STM) and conductive atomic force microscopy (cAFM) to characterize chemically modified epitaxial graphene on SiC(0001) [2,3]. For example, a suite of perylene-based molecules form highly ordered self-assembled monolayers (SAMs) on graphene via gas-phase deposition in UHV [4,5]. Due to their noncovalent bonding, these SAMs preserve the superlative electronic properties of the underlying graphene while providing uniform and tailorable chemical functionality [6]. In this manner, disparate materials (e.g., high-*k* gate dielectrics) can be seamlessly integrated with graphene, thus enabling the fabrication of capacitors, transistors, and related electronic/excitonic devices [7]. Alternatively, via aryl diazaonium chemistry, functional polymers can be covalently grafted to graphene [8], while exposure to atomic oxygen in UHV enables chemically homogeneous and thermally reversible covalent epoxy functionalization [9]. Beyond UHV STM characterization, this talk will also delineate our most recent efforts to exploit chemically modified graphene in technologically significant applications including photovoltaics [10], transparent conductors [11-13], flexible GHz transistors [14], *in vivo* biomedical applications [15,16], and photocatalysts [17].

[1] Q. H. Wang and M. C. Hersam, *MRS Bull.*, **36**, 532 (2011).

[2] J. A. Kellar et al., *Appl. Phys. Lett.*, **96**, 143103 (2010).

[3] J. M. P. Alaboson et al., *Adv. Mater.*, **23**, 2181 (2011).

[4] Q. H. Wang and M. C. Hersam, *Nature Chemistry*, **1**, 206 (2009).

[5] Q. H. Wang and M. C. Hersam, *Nano Lett.*, **11**, 589 (2011).

[6] J. D. Emery et al., *Surf. Sci.*, **605**, 1685 (2011).

[7] J. M. P. Alaboson, et al., *ACS Nano*, **5**, 5223 (2011).

[8] Md. Z. Hossain et al., *J. Am. Chem. Soc.*, **132**, 15399 (2010).

[9] Md. Z. Hossain et al., *Nature Chemistry*, **4**, 305 (2012).

[10] I. P. Murray et al., *J. Phys. Chem. Lett.*, **2**, 3006 (2011).

[11] A. A. Green and M. C. Hersam, *J. Phys. Chem. Lett.*, **1**, 544 (2010).

[12] A. A. Green and M. C. Hersam, *Nano Lett.*, **9**, 4031 (2009).

[13] Y. T. Liang and M. C. Hersam, *J. Am. Chem. Soc.*, **132**, 17661 (2010).

[14] C. Sire et al., *Nano Lett.*, **12**, 1184 (2012).

[15] M. C. Duch et al., *Nano Lett.*, **11**, 5201 (2011).

[16] J.-W. T. Seo et al., *J. Phys. Chem. Lett.*, **2**, 1004 (2011).

[17] Y. T. Liang et al., *Nano Lett.*, **11**, 2865 (2011).

9:40am **GR+AS+BI+PS+SS-WeM6 Structure of a Peptide Adsorbed on Graphene and Graphite**, *J. Katoch,* University of Central Florida*, S.N. Kim, Z. Kuang, B.L. Farmer, R.R. Naik,* Air Force Research Laboratory*, S.A. Tatulian,* ***M. Ishigami***, University of Central Florida

Non-covalent functionalization of graphene using peptides is a promising method for producing novel sensors with high sensitivity and selectivity. We have performed atomic force microscopy, Raman spectroscopy, infrared spectroscopy and molecular dynamics simulations to investigate peptide-binding behavior to graphene and graphite. We studied a dodecamer peptide, GAMHLPWHMGTL, identified by phage display to possess affinity for graphite.

Optical spectroscopy reveals that the peptide forms secondary structures both in powder form and in an aqueous medium. The dominant structure in the powder form is α-helix, which undergoes a transition to a distorted helical structure in aqueous solution. The peptide forms a complex reticular structure upon adsorption on graphene and graphite, having a helical conformation different from α-helix due to its interaction with the surface. Our observation is consistent with our molecular dynamics calculations and our study paves way for rational functionalization of graphene using biomolecules with defined structures and, therefore, functionalities. Our results have recently been published [1].

[1] J. Katoch, S.N. Kim, Z. Kuang, B. L. Farmer, R. R. Naik, S. A. Tatulian, and M. Ishigami, dx.doi.org/10.1021/nl300286k, Nano Letters (2012).

10:40am **GR+AS+BI+PS+SS-WeM9 Controlling the Spatial Distribution of Graphene Chemistry**, ***S.C. Hernández***, *E.H. Lock, S.G. Walton, C.J. Bennett, R. Stine, P.E. Sheehan, F.J. Bezares, L.O. Nyakiti, R.L. Myers-Ward, J.T. Robinson, J.D. Caldwell, C.R. Eddy, Jr., D.K. Gaskill*, Naval Research Laboratory

Graphene has attracted a widespread of interest because of its unique structural and electronic properties however, manipulation of these properties is necessary before realizing its full potential as the next generation material in a broad range of applications. Precise control of the surface chemistry of graphene can allow for subsequent surface procedures both for device fabrication (i.e. atomic layer deposition) and sensor applications. Chemical composition strongly impacts the electronic properties as well as chemical reactivity, both globally and locally. Electron-beam generated plasmas are capable of imparting a variety of functional group types over a range of coverages with minimal damage to the carbon back bone because of their inherently low ion energies and as such offer a unique approach for large area uniform processing of graphene films with controlled surface chemistry. The ability to manipulate the surface chemistry of this atomically thin material coupled with the capability to regulate the spatial distribution of functional will be discussed. Plasma processing conditions and characteristics, as well as the resulting chemical, structural, and electrical properties of the functionalized graphene will be demonstrated. This work is supported by the Naval Research Laboratory base program.

11:00am **GR+AS+BI+PS+SS-WeM10 Coverage-dependent Ordering of Adsorbed Iron Phthalocyanine on Epitaxial Graphene Grown on SiC(0001)-Si**, ***A.A. Sandin***, *D.B. Dougherty, J.E. Rowe*, North Carolina State University

The crystallographic and electronic structure of monolayer and sub-monolayer Iron-Phthalocyanine (FePc) films are experimentally studied on graphene grown on SiC(0001) using Scanning Tunneling Microscopy and Spectroscopy (STM and STS) as well as Low Energy Electron Diffraction (LEED). At full monolayer coverage of FePc the STM images show that a nearly square overlayer lattice forms with flat-lying molecules and a densely-packed structure oriented 10° relative to the graphene principle lattice directions. This close-packed structure i appears to be the same as that previously reported for FePc on graphite surfaces. For sub-monolayer coverage at room temperature, our STM images suggest that FePc forms a unique 2D molecular gas with images that have the hexagonal symmetry of the graphene honeycomb lattice. This is interpreted as suggesting that only a small diffusion barrier exists for molecular motion between neighboring sites in the 3-fold symmetry of the sub-monolayer overlayer lattice. The sub-monolayer gas condenses into islands at liquid Nitrogen temperatures with bare graphene regions and this implies that a weak attractive interaction exists between FePc molecules causing the close-packed ordering. Near defects in the graphene lattice we observe ring-like structures at room temperature that suggest an increased residence time of the mobile 2-D gas of FePc molecules. Our results using Scanning Tunneling Spectroscopy suggest the possibility of a hybrid molecule-graphene state in the unoccupied density of both states near the Fermi level which could possibly be useful in modifying the charge injection into graphene in future devices.

11:20am **GR+AS+BI+PS+SS-WeM11 A Molecular Route to Carbon Nanomembranes, Graphene and Their Hybrids with Tailored Physical and Chemical Properties**, ***A. Turchanin***, University of Bielefeld, Germany **INVITED**

Bottom-up approaches via molecular self-assembly have high potential to facilitate the applications of two-dimensional (2D) carbon materials in nanotechnology. In this talk it will be demonstrated how self-assembled monolayers (SAMs) of aromatic molecules can be employed to this end. These monolayers are converted into *carbon nanomembranes* (CNMs) with a thickness of one molecule by electron or photon irradiation. CNMs can be separated from their original substrates and transferred onto various other substrates, fabricated as suspended nanomembranes or stacked into multilayer films with precise control over their thickness and composition. They possess two chemically distinct faces, which can be used for their selective functionalization, opening broad avenues for the engineering of novel materials with tailored on demand properties. High temperature annealing induces the transformation of CNMs into *graphene*, which allows large-area fabrication of the homogenous sheets with tunable electrical, optical and chemical properties. Integration of graphene sheets with CNMs into novel hybrids presents a promising route to flexibly functionalize graphene for applications as optical, electrical, chemical and biofunctional coating in nanoelectronics and sensors. Various physical and chemical properties of these novel materials, their nanopatterning and functional applications will be presented.

1) A. Turchanin and A. Gölzhäuser, *Prog. Surf. Sci.* (2012) in press.

2) A. Turchanin, D. Weber, M. Büenfeld, C. Kisielowski, M. Fistul, K. Efetov, R. Stosch, T. Weimann, J. Mayer, A. Gölzhäuser, *ACS Nano* 5 (2011) 3896-3904.

3) C.T. Nottbohm, A. Turchanin, A. Beyer, R. Stosch, A. Gölzhäuser, *Small* 7 (2011) 874-883.

4) Z. Zheng, C.T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Gölzhäuser, *Angew. Chem. Int. Ed.* 49 (2010) 8493-8497.

5) A. Turchanin, A. Beyer, C.T. Nottbohm, X. H. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Gölzhäuser, *Adv. Mater.* 21, 1233-1237 (2009).

Plasma Science and Technology
Room: 24 - Session PS+TC-WeM

Atmospheric Plasma Processing for PV, Flexible Electronics (incl. R2R)
Moderator: S.A. Vitale, MIT Lincoln Laboratory

8:00am **PS+TC-WeM1 Formation Dynamics and Characterization of Organosilicon Powders in Microwave-Sustained Plasmas at Atmospheric-Pressure**, *V. Roy-Garofano*, ***A. Kilicaslan***, *O. Levasseur, L. Stafford, M. Moisan,* Universite de Montreal, Canada, *C. Côté, A. Sarkissian*, Plasmionique, Canada

An atmospheric-pressure plasma sustained by a propagating electromagnetic surface wave in the microwave regime combined with a bubbler/flash evaporator developed by Plasmionique for the injection of liquid precursors was used to generate organosilicon powders. Analysis of the plasma emission revealed the apparition of strong C_2 (Swan system) and CN emission bands along with Si emission lines following the addition of the hexamethyldisiloxane (HMDSO) precursors in the nominally pure argon plasma. Such features were not observed in atmospheric-pressure Ar/HMDSO discharges controlled dielectric barriers, indicating that microwave-sustained plasmas are characterized by much higher precursor fragmentation levels due to their much higher electron density. The emission spectra further showed a high-intensity continuum, the intensity of which decreased with time as powders started to form on the discharge tube walls. Analysis of the powder chemical composition by Fourier-Transform Infrared Spectroscopy showed very strong Si-$(CH_3)_x$ and O-Si-$(CH_3)_x$ bands, consistent with the formation of a silicon carbide. On the other hand, introduction of trace amount of O_2 in Ar/HMDSO produced white powders with strong Si-O-Si bands and no trace of carbon, consistent with the formation of SiO_x.

8:20am **PS+TC-WeM2 Infrared Gas Phase Studies in High-Current Dielectric Barrier Discharges Applied in Roll-to-Roll Deposition of Silica-Like Layers at Atmospheric Pressure**, ***S. Welzel***, Eindhoven University of Technology, Netherlands, *S.A. Starostin, H. de Vries,* FUJIFILM Manufacturing Europe B.V., Netherlands, *M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, Netherlands

Large-area plasma-enhanced roll-to-roll processing of polymeric substrates in diffusive dielectric barrier discharges (DBDs) have been shown to yield high-quality SiO_2-like barrier layers. This has been obtained through chemical vapour deposition at atmospheric pressure using organo-silicon precursors (HMDSO or TEOS) and industrially relevant air-like gas mixtures (N_2/O_2/Ar). Provided an electronic stabilisation circuit is applied, high currents in different diffusive discharge modes can be achieved without admixtures of Helium. Earlier, extensive surface analysis studies of the synthesised layers revealed a competion between deposition and etching regimes throughout the active plasma zone and led to the development of a deposition model.

This contribution is concerned with complementary studies of the gas phase composition using infrared absorption techniques. Given the challenging optical access to DBDs with gap distances smaller than 1 mm in industrial-like roll-to-roll configuration a gas sampling system was implemented to collect a fraction of the effluent into a multiple pass absorption cell. Main stable products were identified under various discharge conditions such as different O_2 admixtures and (average) power densities. Broadly speaking, a typical H-N-O chemistry in the presence of traces of hydrocarbons is observed for such high-current DBDs. To establish a link to earlier model assumptions both dominant etching and deposition conditions were studied separately (i.e. precursor absent and added, respectively). Formic acid (HCOOH) was found to be a good marker molecule in the gas phase for strong etching of the polymeric substrate or incomplete precursor dissociation. Particularly, the appearance of precursor fragments in the infrared gas phase spectra can be correlated to the injected power and growth rate. Under conditions of complete precursor depletion the effluent zone of the reactor resembles an air-like plasma where NO_2, NO, N_2O and HNO_2 are observed whilst hydrocarbons or alcohols are absent.

8:40am **PS+TC-WeM3 Atmospheric Pressure Plasma Processes for Preparation of Si-Based Thin Films**, ***K. Yasutake***, *H. Ohmi, T. Yamada, H. Kakiuchi*, Osaka University, Japan **INVITED**

Thin-film deposition processes using atmospheric-pressure (AP) plasmas have attracted considerable attention as the low-cost deposition methods, because they can realize low-temperature and high-rate deposition without the necessity for ultrahigh vacuum. Recently, we have demonstrated that good-quality Si films with almost no ion damage can be prepared by using a 150-MHz very high-frequency AP plasma. Based on this result, we are studying applications of AP plasmas in semiconductor processing, e. g., i) atmospheric-pressure plasma chemical vapor deposition (AP-PCVD) of semiconductor and insulator thin films, ii) AP plasma oxidation of Si and Al, and iii) atmospheric-pressure plasma enhanced chemical transport (APECT) processes for Si purification and deposition. In this work, we will report the experimental results on the formation and characterization of Si-based thin films prepared by these AP plasma processes.

Firstly, we have studied the epitaxial Si growth by AP-PCVD. The purpose of the study is to develop a totally low-temperature semiconductor device fabrication process. Epitaxial Si films have been prepared on 4-inch-(001) Si wafers by AP-PCVD using a porous-carbon electrode. Defect-free growth of epitaxial Si is confirmed in the temperature range of 470–570°C by transmission electron microscopy and a selective etching method. A high carrier generation lifetime (≈ 2.0 ms) is observed in the Si film grown at 570°C with a reasonably high growth rate (≈ 0.4 μm/min). *In situ* H_2 plasma cleaning of the substrate surface is effective for eliminating O and C concentration peaks at the film/substrate interface. Heavy B doping with a carrier concentration of about 10^{20} cm^{-3} is achieved using B_2H_6 as a doping gas at 570°C. The relation between the mobility and carrier concentration in p- and n-doped Si films can be well fitted by the reported curves for bulk Si single crystals. These results demonstrate that the electrical quality of Si epitaxial films grown by AP-PCVD is sufficiently good for semiconductor device applications.

One of the other topics is on the AP plasma oxidation of Si. AP plasma oxidation is supposed to be most compatible for a chamber-less and open-air process, which is attractive as a high-throughput oxidation process for photovoltaic applications. SiO_2/Si structures have been prepared by AP plasma oxidation at 400°C using gas mixtures of O_2 and He. Various characterization results reveal that the properties of AP plasma oxides are similar to those of high-temperature thermal oxides, and that the SiO_2/Si structure has a low interface state density of the order of 10^{10} $cm^{-2}eV^{-1}$.

9:20am **PS+TC-WeM5 Deposition of Organic-Inorganic Nanocomposite Coatings by Aerosol-Assisted Atmospheric Pressure DBDs**, ***F. Fanelli***, Institute of Inorganic Methodologies and Plasmas (IMIP) - CNR, Bari, Italy, *A.M. Mastrangelo, F. Fracassi*, University of Bari Aldo Moro - IMIP CNR, Bari, Italy

Aerosol-assisted atmospheric pressure cold plasma processes have been recently addressed as an attractive route towards the deposition of multifunctional coatings. This approach seems to be particularly convenient, and can even offer the only possible solution, when non-volatile precursors, solutions or dispersions need to be injected directly in the atmospheric plasma. The aerosol of a dispersion of nanoparticles (NPs) in a liquid precursor can lead to the deposition of nanocomposite coatings in which the NPs are embedded in the matrix formed by the plasma polymerization of the precursor.

This contribution is focused on the study of the growth and structure of plasma-deposited polyethylene/zinc oxide (PE/ZnO) nanocomposite coatings with several potential applications due for instance to the UV-protection and photocatalitic properties of ZnO.

The coatings are deposited in a parallel plate dielectric barrier discharge (DBD) fed with He and the aerosol of a dispersion of oleate-stabilized ZnO NPs in octane or octane/1,7-octadiene mixtures. The characterization of the coatings is performed using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), water contact angle (WCA) goniometry.

A comprehensive study on the effect of different process parameters (e.g., atomization conditions, dispersion composition in terms of liquid precursor and ZnO NPs concentration, deposition time) on the chemical composition and structure of the film will be presented.

Preliminary results show that, as expected, with increasing the concentration of ZnO NPs in the starting dispersion from 0.5 to 5% p/p, the ZnO content in the coating increases. Surprisingly, the addition of a small amount of 1,7-octadiene to octane (0.5% v/v) favors the inclusion of the NPs and hence results in an increase of the ZnO concentration of the coatings.

Advancing and receding WCAs steeply increase with the NPs content in the film and reach values higher than 165° with low hysteresis indicating the formation of slippery superhydrophobic surfaces. SEM images confirm that this superhydrophobic character is due to the hierarchical micro-/nano-structured surface morphology of the coatings. ZnO NPs generally aggregate in almost spherical clusters that can be incorporated to a different extent into the polyethylene-like matrix as a function of the deposition process conditions.

10:40am **PS+TC-WeM9 Modified Dielectric Barrier Discharges for Display Materials Processing**, *G.Y. Kim,* Sungkyunkwan University, Korea, *J.B. Park,* SKKU Advanced Institute of Nano Technology (SAINT), Korea, ***G.Y. Yeom***, Sungkyunkwan University & SKKU Advanced Institute of Nano Technology (SAINT), Korea **INVITED**

Atmospheric pressure plasmas have been investigated tens of years for the application to semiconductor and display processing. Especially, due to the uniform discharge characteristics, dielectric barrier discharges (DBDs) composed of electrodes covered with dielectric material have been investigated intensively for those applications. In our study, the conventional DBDs have been modified to enhance the plasma density and also, the different types of DBDs such as remote-type DBD and hybrid-type DBDs (which is composed of direct-type DBD and remote-type DBD) have been used for the surface treatment, growth, deposition, and etching of material applied to flat panel displays and their effects on the material processing have been studied. In this presentation, I will present the plasma characteristics and materials characteristics obtained with those different types of modified DBDs and will suggest possible applications of the DBD-type atmospheric pressure plasmas for the next generation display processing such as in-line/roll-to-roll processing, flexible display substrate processing, inkjet processing, etc.

11:20am **PS+TC-WeM11 Etching of PTFE by Atmospheric Plasmas: Effect of the Gas Composition on the Reactions Processes and Hydrophobicity**, ***J. Hubert****, *T. Dufour, N. Vandencasteele,* Université Libre de Bruxelles, Belgium, *S. Desbief, R. Lazzaroni,* Materia Nova Research Center, Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

Poly(tetrafluoroethylene) (PTFE) is a hydrophobic material due to its fully fluorinated backbone (-CF2-CF2-), with properties interesting for practical applications such as self-cleaning surfaces. It has been shown that super-hydrophobic surfaces can be obtained by the treatment of PTFE in a helium-oxygen plasma at atmospheric pressure [1]. Contrary to oxygen-containing plasmas, the modification of PTFE by a pure helium plasma at atmospheric pressure usually leads to a strong decrease in water contact angle, in addition to an oxygen incorporation [2].

The treatment of PTFE by the atmospheric post-discharge of an RF plasma torch supplied in He and He-O2 highlighted two totally different behaviors [3]. For this reason, the effect of the gas composition (ratio He/O2) on the polymer modifications has been investigated. The treated surfaces have been characterized by WCA, XPS and AFM. Moreover, the species responsible for the modifications have been identified by optical spectroscopies (OES/OAS).

In pure helium plasmas, no significant change of the surfaces regarding chemical composition (XPS), wettability (WCA) and morphology (AFM) has been observed and this, despite an important mass loss measured. According to these observations, we presume a layer-by-layer physical etching without any preferential orientation, where the highly energetic helium metastables should be the main species responsible for the scission of -(CF2)*n*- chains. The XPS analysis of an aluminum foil (known to be an

* Coburn & Winters Student Award Finalist

efficient fluorine trap) placed close to the PTFE tends to confirm this assumption as fluorine atom and –CF2 fragments have been detected.

In He-O2 plasmas, the helium metastables species being consumed by oxygen, fewer of them are then available to etch the PTFE, reducing the mass losses and fluorine detection on aluminum for higher O2flow rates. However, as it was previously shown [2], WCA and AFM measurements indicate an increase in hydrophobicity and roughness of the PTFE surface. The alveolar structures observed by AFM are then assumed to come from the anisotropic etching where the atomic oxygen etches mainly the amorphous phase.

[1] T. Dufour, J. Hubert, P. Viville, C.Y. Duluard, S. Desbief, R. Lazzaroni, F. Reniers, PTFE surface etching in the post-discharge of a scanning RF plasma torch: evidence of ejected fluorinated species, *Plasma Process. Polym.*. 2012, DOI. 10.1002 /ppap.201100209.

[2] **N. Zettsu, H. Itoh, K. Yamamura,***Thin Solid Films*, 2008, 516,6683.

[3] J. Hubert, T. Dufour, N. Vandencasteele, S. Desbief, R. Lazzaroni, F. Reniers, Etching processes operating on a PTFE surface exposed to He and He-O2 atmospheric post-discharges. (Accepted : *Langmuir*).

11:40am **PS+TC-WeM12 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition of Hydrophobic Thin Film Coatings Using Liquid Precursors**, ***J. Yim***, *V. Rodriguez-Santiago, A. Williams, J. Hirvonen, D. Pappas*, U.S. Army Research Laboratory

Hydrophobic coatings are known to impart self-cleaning, anti-fouling, anti-fog and wicking properties on polymeric substrates and textiles. These coatings are largely derived from either wet chemical methods or low pressure plasma-based chemical vapor deposition techniques using gaseous precursors. In an effort to eliminate the use of large quantities of chemicals and solvents associated with wet chemistries and to deter the use of costly vacuum systems, we explored the practicality of an atmospheric pressure plasma jet (APPJ) as a comparable alternative to low pressure plasma systems. To obtain coatings typically achieved through wet chemistry, and often limited by commonly used fluorocarbon gases such as C_3F_6, liquid fluorinated precursors such as fluoroalkyl silanes (FAS) were explored. FAS with varying fluorocarbon chain lengths were studied and deposition conditions as a function of electrode-substrate gap distance, deposition time and power were investigated. Ultra high molecular weight polyethylene (UHMWPE) films served as the model polymer system in which the coatings were deposited owing to its simple molecular structure consisting of $-CH_2-CH_2-$ chains. The characteristic properties of the coatings on UHMWPE such as hydrophobicity, chemical composition, uniformity and deposition rates were studied to establish a correlation between processing parameters and the coating properties. X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements confirmed the presence of CF, CF_2, and CF_3 functionalities in the coating composition and reveal that there is a strong dependence of these groups on the chain length of fluorocarbon groups in the FAS precursors. Water contact angle (WCA) measurements confirm hydrophobicity of the coating, where angles over 90° were recorded. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques were utilized to probe the morphological profiles of the coatings. Profilometry and ellipsometry show deposition rates of the coating ranging from nanometer to sub-micrometer thick coatings. Results show that the use of APPJ with liquid precursors is promising in achieving hydrophobic coatings under atmosphere without producing large volumes of hazardous waste.

Plasma Science and Technology
Room: 25 - Session PS-WeM

Advanced BEOL/Interconnect Etching
Moderator: A. Agarwal, Applied Materials Inc.

8:00am **PS-WeM1 The Role and Impact of Metal Hard Masks on BEOL Etch Processes**, ***C. Labelle***, *R. Srivastava, R. Koshy, T.Q. Chen, F. Wu, A.P. Labonte,* GLOBALFOUNDRIES, *Y. Mignot,* STMicroelectronics, *M. Beard, B.G. Morris, Y. Yin*, IBM Systems and Technology Group **INVITED**

Back-End-of-Line (BEOL) etch processes have undergone a significant transition in recent years as the requirements of advanced technology nodes have shifted the advantage from via-first-trench-last (VFTL) to trench-first-metal-hard-mask (TFMHM) dual damascene patterning schemes throughout the industry. This shift has been primarily driven by the TFMHM scheme's ability to enable self-aligned vias (SAV), as well as inherently be more multi-patterning friendly through the use of a dissimilar hard mask material. However, typically key advances don't come without other complexities, and TFMHM is no exception. The role and impact that the metal hard mask material has on all of the etches where it is involved is significant and sometimes very subtle. At a high level, the metal hard mask influences can be split into two areas: patterning of the MHM itself, and etches where the material acts as the hard mask. The patterning of the MHM itself is where all of the challenges associated with multi-patterning come into play. The MHM profile largely determines the overall critical dimension behavior across all patterns, and so pattern control and fidelity in both x and y dimensions are critical. The material properties of the MHM play a significant role in etch profile control and line edge/width roughness (LER/LWR). When considered as a hard mask in the etch, the MHM impacts are far-reaching. First, the selectivity of the MHM material vs. the underlying films must be considered. This is a key focus of etch process optimization when implementing an SAV patterning scheme and often drives all facets of the etch process. Second, the very properties that make it attractive as a hard mask (etch resistivity) can also make it the source of many other issues, typically due to the non-volatile nature of most MHM materials (Ti, TiN, TaN, etc.). Some examples include metal-containing sidewall and/or via hole residues, temperature sensitive profiles, ability to shape the MHM to help metallization, and chamber contamination effects (i.e., non-repeatability or slot-order effects). The MHM material properties have a large influence on these etches, as well, with tradeoffs between etch resistivity (good for SAV) and metal material stress (bad for pattern integrity --> can induce line wiggling). This talk will review some of the benefits of utilizing a metal hard mask, as well as some of the challenges that come hand-in-hand with it and how plasma etch process optimization is advancing in learning how to work with these materials.

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

8:40am **PS-WeM3 Evaluation of Chemistry Effects of Fluorcarbon Molecules for High Aspect Ratio Silicon Oxide Etch**, ***C.M. Anderson***, *R. Gupta, C. Dussarrat*, Air Liquide

For semiconductor dry etch applications, the evolution of chemistry selection has shifted away from fully saturated fluorocarbons towards molecules that exhibit increased selectivity of silicon oxide over mask and underlayer materials. Recent studies show that the presence of both H atoms and C=C bonds can improve selectivity while maintaining reasonable silicon oxide etch rate. The reason for this is linked to the behavior of molecule fragments in a plasma etch environment, wherein higher C:F ratios are favored. The intent of this work is to systematically study the role of gas molecule structure as it affects etching behavior, with the goal of finding an ideal candidate molecule to enable current and future processing requirements.This study will provide an extensive survey of etch chemistries in order to uncover the specific effects of H, C=C double bonds, F:C ratio, and molecule structure as they relate to etching performance. The model chemistries for this work include both cyclic- and linear-type structures. Using a RIE plasma etch tool, the performance of each molecule is studied on blanket wafers, measuring silicon oxide etch rate as well as selectivity to photoresist, silicon nitride, and amorphous carbon hardmask films. For selected conditions of optimized etch rate and PR selectivity, patterned wafer stacks are also etched and examined in cross-section SEM. Corresponding optical emission spectroscopy (OES) data is collected at the same time, showing qualitatively the relative densities of active species in the plasma during the etch process. In order to develop predictive tools to correlate etch performance to the molecule structure, we perform mass spec measurements of the gases by direct injection of the fluorocarbon gas, measuring the electron-impact fragmentation of each gas. Electron energies from 10-100 eV are recorded, and the relative abundance of each fragment species is plotted against the electron energy. It is found that this method gives a strong indication of a molecules propensity to deposit polymer films during an etch process. Further, the nature of the representative polymer film for each gas can be predicted from the fragmentation patterns, in terms of F:C ratio and C-F bonding as measured by XPS.As a result of this analytical work, several optimum etch molecules have been identified that exhibit excellent selectivity to both PR and a-C hardmask. These chemistries are currently being tested in commercial dielectric etch tools to validate performance.

9:00am **PS-WeM4 Dielectric RIE Challenges Associated to Trench First Metal Hard Mask at 64 nm Pitch and Below**, ***Y. Feurprier***, *L. Wang,* Tokyo Electron Tech. Center, America, LLC, *S. Nakamura,* Tokyo Electron Miyagi Ltd., Japan, *J. Stillahn, Y. Chiba, K. Kumar,* Tokyo Electron Tech. Center, America, LLC, *Y. Mignot,* STMicroelectronics, *E. Soda,* Renesas Electonics, *R. Koshy, R. Srivastava,* GLOBALFOUNDRIES, *Y.J. Park,* Samsung Electronics Co. Ltd., *J. Arnold*, IBM Research Group

Over the last couple of technology nodes (from 45 nm node and beyond), Trench First Metal Hard Mask (TFMHM) integration scheme has gained traction and become the preferred integration of low-k materials for BEOL. This integration scheme also enables Self-Aligned Via (SAV) patterning

which prevent via CD growth and confines via by line trenches to better control via to line spacing. Also for the 64 nm pitch technology and below, TFMHM is well suited for double patterning of the line definition required for the ever smaller line pitches of the most critical BEOL levels. In the SAV process, temperature, gas chemistry, power and pressure were shown to be key process parameters to meet the metal HM selectivity requirements. The flexible adjustment of the ion energy and control of the flux of ions and active neutrals was shown to be critical to meet the metal HM selectivity requirements for both SAV and trench etching. The TFMHM integration at these dimensions requires careful and controlled metal HM selectivity. These tight technology requirements at these ever smaller pitches also challenge hardware to bring evolutionary improvements to enable wider process windows to meet tighter process specifications. In this paper, the RIE efforts on process controls of the via and trench profiles, the metal HM selectivity management and hardware solutions to address the dielectric RIE challenges associated to TFMHM scheme at 64 nm pitch and below will be discussed.

This work was performed by the Research and Development team at TEL Technology Center America in joint development with IBM Research Alliance Teams in Albany, NY 12203.

This work has also been supported by the independent Bulk CMOS and SOI technology development projects at the IBM Microelectronics Div. Semiconductor Research & Development Center, Hopewell Junction, NY 12533.

9:20am **PS-WeM5 Interfacial Characterization of Patterned Porous Low-k Nanostructure using Infrared and X-ray Photoelectron Spectroscopy**, *S. Rimal, N. Ross, S. Koskey, T. Mukherjee,* ***O. Chyan***, University of North Texas

The advanced microelectronic architecture utilizes more conductive Cu interconnect insulated by porous low-k interlayer dieelctrics (ILD) to minimize the overall RC delay. To decrease the dielectric constant, the porosity of organosilicate glass was increased by partial replacing Si-O with Si-C bonds during plasma-enhanced chemical vapor deposition. However, carbon stripping by subsequent plasma etching/patterning processes can make porous low-k interlayer dielectrics, with higher carbon content, more prone to water damage during subsequent wet cleans processes. In this presentation, we report the development of a new characterization approach that utilizes Multiple Internal Reflection Infrared Spectroscopy (MIR-IR) as a sensitive characterization tool to guide the development of cleans-friendly plasma etches with minimal ILD damages. Previously, we have successfully utilized MIR-IR to characterize chemical bonding of hydrogen termination, trace organic adsorption and plasma deposited polymer thin film on silicon wafer surface with sub-monolayer sensitivity. MIR-IR utilizes the silicon wafer (including patterned ILD wafer) itself as an IR waveguide to enable multiple total internal reflections which greatly enhances IR measuring sensitivity. Therefore, MIR-IR possesses a unique capacity of identifying specific functional groups of deposited thin films (sub 10 nm) and monitoring their corresponding reactivity evolution influenced by plasma process. We will discuss new characterization results of post-etch residues formation (fluoro-polymers), plasma etch induced water damage (silanols formation) and oxygen plasma etch of organic thin film on patterned porous low-k nanostructure using MIR-IR spectroscopy, x-ray photoelectron spectroscopy and other surface characterization techniques.

9:40am **PS-WeM6 Separation of Radical and Photon Effects on Nanoporous Low-*k* Films**, ***J. Lee*****, *D.B. Graves*, University of California Berkeley

Porous low-*k* materials are highly susceptible to damage from plasma species during various stages of plasma processing. Oxygen plasma, possibly the most damaging, causes significant carbon loss throughout the film, making the material hydrophilic. Absorption of water results in an increase in the dielectric constant and degradation of dielectric properties. Various O_2 plasma species, such as oxygen radicals (O) and vacuum-ultraviolet (VUV) photons, can be shown to cause this carbon loss. Separation of these species to analyze individual effects can be achieved by covering the sample with a MgF_2 window to allow only VUV photons to pass or by placing the sample out of the line-of-sight of the plasma to obtain radical effects, since radicals are able to diffuse to, and into, the porous material. By doing this, we can analyze the carbon loss for each individual specie through bulk measurements using Fourier-transform infrared (FTIR) spectroscopy and compare them to uncovered, direct O_2 plasma exposures. Dilute HF dip etches only C-depleted SiO_2, allowing a measure of the depth of C removal by radicals or VUV photons. Oxygen radicals create a nearly C-free modified layer that deepens at a rate proportional to exposure time and that increases with pressure, presumably because of the increase in O density. By contrast, VUV photons travel fairly deep into the film due to relatively low absorption cross-sections, so photon effects gradually occur throughout this penetration depth at a slower rate. Yet, VUV photons alone do not directly result in carbon loss; molecular oxygen is also needed to form volatile species for permanent removal. The results clearly show that radicals and VUV photons generate the damaged layer in different ways and at different rates.

11:00am **PS-WeM10 Evaluation of Novel Etch Gas for BEOL Interconnect Pattern Transfer at 14nm and 22nm Technologies**, ***R.L. Bruce***, IBM T.J. Watson Research Center, *T. Suzuki, M. Nakamura,* Zeon Chemicals L.P., *S. Engelmann, E.A. Joseph, E.M. Sikorski, N.C.M. Fuller,* IBM T.J. Watson Research Center, *A. Itou*, Zeon Corporation

As feature sizes continue to decrease, significant issues are found using high selectivity fluorocarbon gases to etch interconnect low-k dielectrics including low selectivity to organic masks, line wiggling and low-k damage. We have evaluated novel etch gases that enables the optimized fabrication of BEOL interconnects for 14nm and 22nm nodes. Compared to conventional fluorocarbon etch gases, experiments with a novel hydrofluorocarbon etch gas have shown a substantial increase in low-k dielectric etch selectivity to organic hard mask and improved selectivity to the capping layer. In addition, lower line-edge and line-width roughness values were observed. We investigate the etch behavior and selectivity between the low-k dielectric and organic hard mask, metal hard mask, and capping layer through optical emission spectroscopy and x-ray photoelectron spectroscopy. Etch performance is assessed for trench and via patterns and also full dual-damascene structures. Low-k damage is also investigated by post-etch HF treatment to measure critical dimension loss from dissolution of plasma-damaged dielectric. Finally, we propose a mechanism for high selectivity, low damage dielectric etch at sub-80nm pitch structures using rationally-designed novel etch gases.

11:20am **PS-WeM11 Dry Etching Characteristics Related to TiN Material Properties**, ***A.P. Labonte***, *F. Wu, V. Arunachalam, S. Patil,* GLOBALFOUNDRIES, *C. Niu,* ST Microelectronics, France, *T.Q. Chen,* GLOBALFOUNDRIES, *E. Wornyo, B.G. Morris, Y. Yin,* IBM Microelectronics, *Y. Mignot*, ST Microelectronics, France

TiN is ubiquitous as a hard mask layer in semiconductor patterning applications. Deposition parameters such as DC power, N_2 flow, Ar flow, temperature, pressure, and target to wafer spacing influence the film properties: density, film stress, resistivity, roughness, grain size and uniformity. These changes in the TiN film properties can affect etch characteristics. For TiN hard mask etches, shifts in etch rate, sidewall angle, undercut/gouge, CD control and LER have been observed. For dielectric etches using the TiN layer as a hard mask, changes in selectivity, erosion rate, etch byproducts, CD control, profile angle and pattern loading have been observed. This presentation will show data on the etch behavior of TiN etch as well as the etch when TiN is used as a mask.In a TiN hard mask open application, a uniformly dense film is required. As part of an evaluation of different TiN films, both uniform and non-uniform density TiN films were generated. Changes in deposition conditions were used to adjust film density uniformity while maintaining average film density. The etch process used to pattern these films was a two step process consisting of an end-pointed main etch and a timed over-etch. The impact to the dry etch process of the film change, was to alter the behavior of the two etch steps in radically different ways. For the main etch, the sidewall angle and etch rate were impacted. For the over-etch chemistry, lateral etch-rate, CD control and profile were most impacted. In addition, the impact of pattern density on via CD definition has been studied for a via double patterning scheme employing TiN as a hard mask for part of the etch. The etch was found to behave differently as a function of pattern density in a fluorine-based plasma, which was theorized to be a consequence of redeposition of TiFx etch byproducts. This theory was supported by data showing a series of TiN films with different material properties resulted in different pattern density responses. The selectivity between the TiN and the underlying film being etched was changed by these TiN film changes, resulting in the different behavior.This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

* Coburn & Winters Student Award Finalist

Plasma Science and Technology
Room: 24 - Session PS1-WeA

Plasma Diagnostics, Sensors and Control 2
Moderator: R. Ramos, LTM, France

2:00pm **PS1-WeA1 ECR Plasma Etching Characterization using a Retarding Field Energy Analyzer**, ***B. Dolinaj***, Dublin City University, Ireland, *V. Milosavljevic*, Dublin City University, *D. Gahan*, Impedans Ltd., *N. MacGearailt*, Intel Corporation, *M.B. Hopkins*, Impedans Ltd., *S. Daniels*, Dublin City University

Dry etching technology was introduced to integrated circuit manufacturing due to its unique ability to do anisotropic removal of material to create high aspect ratio structures. Dry etching tools in the semiconductor industry use plasma to generate electrons, bombarding ions and free radicals. These radicals are chemically reactive and highly efficient at removing material from substrate surfaces, so the etch profiles depend on ion density and ion energy.

Electron cyclotron resonance (ECR) plasma etching reactors are widely used in wafer production. They use a low pressure, high density plasma source that has resonant magnetic field coils and two independently controlled microwave and radio frequency (RF) sources. ECR plasma etching is a very complex process and most of the progress with ECR etching tools up to this time has been accomplished empirically. Introducing new and adapted plasma diagnostic techniques is essential for further characterization and better understanding of plasma and etching processes.

In previous work we presented electrical measurements obtained using a retarding field energy analyzer (RFEA) installed in an commercial ECR etching reactor. RFEAs are generally used for charged particle flux and energy distribution measurements at electrically grounded surfaces. We demonstrated that an electrically isolated RFEA can be successfully used for measuring ion energy distribution functions (IEDFs) at the surface of RF driven electrodes in the presence of strong DC magnetic fields.

In this work we present further achievements in plasma diagnostics and ECR etching characterization. The original experimental setup is expanded for additional diagnostic tools. Phase resolved optical emission spectroscopy (PROES) measurements are taken at three different discharge locations simultaneously with RFEA measurements. Electrical and optical measurements show strong correlation in comparable aspects which proves their validity and together they provide more information about plasma in complementary aspects. The RFEA has also been used to measure the electron energy distribution function (EEDF) with the aim of electron temperature and density estimation in the bulk plasma. For validating EEDFs obtained with the RFEA, we performed similar measurements of EEDFs in a capacitively coupled plasma (CCP) reactor using the RFEA and the Langmuir probe. Results of this validation and estimations made from EEDFs are presented and discussed. Experimental and theoretical plasma etching characterization has been done through the analysis of spatially resolved data sets obtained from RFEA and spectroscopic ellipsometry at various radial locations.

2:20pm **PS1-WeA2 Time Resolved Ion Flux Measurement in Pulsed ICP Plasmas**, ***G. Cunge***, *M. Darnon*, LTM-CNRS, France, *N.St. Braithwaite*, The Open University, UK, *E. Despiau-Pujo, P. Bodart, M. Brihoum, M. Haass, O. Joubert*, LTM-CNRS, France

Pulsed ICP plasmas are a promising solution to several technological issues related to IC circuit fabrication. Recent results are indicating that pulsing the inductively coupled power and/or the RF biasing power allows to increase the etch selectivity and to reduce plasma induced damages in ultrathin layer. However, the reasons for these improvements remain unclear. In particular, the impact of plasma pulsing on the ion flux (and ion energy) in electronegative gases used for IC circuit fabrication has not been studied in details. In this work, we have used a capacitively-coupled planar ion flux probe to monitor the time variations of the ions flux in various plasmas (CF4, SF6, Cl2, HBr…etc) operated in an industrial etch reactor from AMAT. We will discuss in detail the experimental set-up that we have designed to carry out time resolved measurement and the issues associated with this measurement. Results will be presented from both electropositive (Ar, He) and electronegative (Cl2, BCl3, SiCl4, SF6) plasmas. We will first present the impact of the ICP source pulsing frequency and duty cycle on the ion flux. These results will be compared to those obtained from a global model. We will then discuss the impact of the RF biasing power on the ion flux in pulsed plasmas. Both the ICP source power and the RF bias power can be independently or synchronously pulsed. In the latter case different duty cycles and a phase delay can be used. During synchronized pulsing with a delay between the ICP and the rf bias pulses, some interesting instabilities (ion flux oscillations) are observed. They are related to the generation of ion acoustic waves by the rapid expansion (or collapse) of the sheath in front of the wafer when the RF bias pulse is applied to the chuck. These results will be eventually compared to IEDF measurements in pulsed plasmas and the consequences on pulsed plasma etch process design will be discussed.

2:40pm **PS1-WeA3 *In Situ* Monitoring of Electron Density and Dielectric Layer on the Wall with Curling Probe**, ***A. Pandey***, *Y. Liang, S. Ikezawa, K. Nakamura, H. Sugai*, Chubu University, Japan

A new type of microwave resonator probe, *curling prob*e, has recently been proposed [1] which employs mono-pole excitation of spiral slot antenna. This probe enables direct measurement of electron density in reactive plasmas, based on a quarter-wavelength resonance at the frequency f=$b(c/4L)[2/(e_{in}+e_{out})]^{1/2}$. Here, b is the finite-size correction factor, L is the antenna length, e_{in} and e_{out} are the relative permittivities of two dielectrics inside and outside the slot antenna, respectively. When the probe is inserted into plasma, the outer dielectric constant e_{out} is expressed as e_p =1-$(f_p/f)^2$ with the electron plasma frequency f_p=$(e^2n/me_0)^{1/2}$. Thus, measuring the resonance frequency of curling probe, one can determine f_p, and hence the electron density n. The finite-difference time-domain (FDTD) simulation of 11-mm-diam curling probe of 35-mm antenna length shows a sharp resonance at the frequency from 1 GHz to 6 GHz uniquely determined by the electron density. The sheath formed in front of the probe surface was modeled as a vacuum layer of ~5l_D in thickness. The resonance frequency was hardly influenced by the sheath at the density higher than 10^{11} cm^{-3}. Basic experiments of electron density measurement by the curling probe were performed in an argon (1~20 Pa) low-power (<2 kW) discharge in ICP device for 300-mm-wafer process. The power dependence of the resonance frequency observed by the curling probe was explained well by the FDTD simulation result as well as the analytical formula. The radial distribution of electron density was measured by a movable curling probe.

When a polymer layer (permittivity e_d) is deposited on the probe surface, the resonance frequency decreases with the increasing layer thickness. Using this probe characteristic, one can *in situ* monitor the thickness of dielectric layer deposited onto a wall of plasma vessel, where the curling probe is positioned to just the same surface of inner wall. The FDTD simulation shows ~10 MHz shift in the resonance frequency for 15-mm-thick deposition of polymer (e_d =3.2), in good agreement with the experimental observation. Thus, the wall deposition layer during chamber cleaning or CVD process can be monitored by the curling probe. In fact, amorphous carbon layer formed on the vessel wall was *in situ* monitored by the curling probe in a 1-kW surface-wave plasma in CH_4/Ar *deposition* discharge and in O_2/Ar *cleaning* discharge. This model experiment successfully demonstrated an applicability of curling probe to monitoring the dielectric layer deposited on the plasma vessel wall.

[1] I. Liang, K. Nakamura, and H. Sugai, Appl. Phys. Express 4, 066101 (2011).

4:00pm **PS1-WeA7 Time Resolved Laser Induced Fluorescence for Probing the Excitation Kinetics of a Low Temperature Argon Discharge**, ***J.M. Palomares Linares***, *E.A.D. Carbone, S. Hübner, W.A.A.D. Graef, J.J.A.M. van der Mullen*, Eindhoven University of Technology, the Netherlands **INVITED**

In this contribution we report a series of experiments based on time resolved laser induced fluorescence (tr-LIF) on low temperature discharges. This technique is used, in combination with Thomson scattering (TS) measurements, to get insight in the excitation kinetics of the discharge.

This method is used to pump different levels within the 4p and 5p groups of the Ar excitation space, from the Ar metastable level $1s_5$. Measuring the tr-LIF decay times in combination with the TS measurements of electron density provides simultaneously total destruction rates by electron and heavy particle collision of the pumped levels. These effective excitation rates are of great importance for the development of models, and are scarce in the case of high excited argon levels.

Similarly, the time response of the collisional induced fluorescence signals (tr-LCIF) emitted by other excited levels is used to study the interaction between levels. In the particular case of Ar this method is used to obtain the "depopulation rates" of metastable 4s levels. When other gasses are introduced in the discharge tr-LCIF signals are obtained from the emission of different excited species of those gasses. These experiments enable us to probe in details the excitation exchange between different species. The use of a high rep-rate system is fundamental for the LCIF measurements, where the low intensity of the signals demands measurement times up to 30 minutes.

The experiments are done in a range of intermediate pressures (0.65 mbar – 40 mbar), on a surfatron microwave induced plasma, working with pure Ar, and mixtures of Ar with H_2, O_2, and N_2. The tr-LIF diagnostic is performed with a 5KHz high rep-rate Nd:YAG laser in combination with a Dye laser system. This setup allows to record tr-LIF signals 500 times more intense than with the common 10 Hz systems. Two equivalent systems are used to pump different wavelengths, a tripled frequency Nd:YAG (@355 nm) in combination with a Coumarine-2 Dye laser (430 nm - 460 nm), and a doubled frequency Nd:YAG (@532 nm) with a Pyridine-1 Dye laser (670 nm – 720 nm). The Thomson scattering measurements are performed with an independent Nd:YAG (532 nm) system and a triple grating spectrograph for the detection of the scattered photons.

4:40pm **PS1-WeA9 Analysis of Run-to-Run Variability in the Bosch Process using rf Probe and Emission Spectroscopy Measurements***, **M. Fradet**, L. Stafford,* Université de Montréal, Canada*, C. Coïa*, Teledyne Dalsa, Canada

Deep silicon etching is a crucial step for several emerging and evolving technologies, including micro-electromechanical systems (MEMS) and CMOS image sensors. Among etching methods available, the Bosch process is widely used because it allows fast etching rates together with high aspect ratios. This process relies on rapidswitches between isotropic etching in SF_6-containing plasmas and polymer deposition for sidewall passivation in C_4F_8-containing plasmas. As a result of reactor wall conditioning, run-to-run variability in etching rates and uniformity is commonly observed. In order to understand the origin of such drifts and thus to develop new strategies to reduce these effects, we have started investigations of the temporal evolution of the properties of SF_6 and C_4F_8 plasmas in the Bosch process on an industrial, inductively-coupled plasma reactor (ICP) at Teledyne Dalsa. In this context, a rf probe was installed on the transmission line connecting the generator to the substrate holder. This system measures the amplitude of the current and voltage as well as the phase between them, allowing determination of the real and imaginary parts of the impedance. During one etch cycle in Ar/SF_6 (total duration of 10s), the absolute value of the reactance, |X|, decreased sharply within the first second and then reached a plateau. For one sample exposed to many etch and deposition cycles, the cycle-averaged value of |X| slowly decreased between the first and the 70th cycle. For many samples etched in the same chamber with a 2 minutes O_2 plasma clean between each run, the run-averaged value of |X| decreased with the sample number. Over this whole range of experimental conditions, the resistance remained fairly constant. From optical profilometry measurements, the etching rate was found to decrease from 340 to 300 nm/s between run #1 and #5. This decrease matched relatively well the observed decrease of |X|, suggesting that the reactance determined from rf probe measurements is a good parameter to examine in a non-intrusive way run-to-run variability in deep silicon etching. More recently, preliminary analysis of the plasma emission in the Ar/SF_6 plasma revealed that the F (703.7 nm)-to-Ar (750.4 nm) line-intensity ratio (related to the F density) remained constant within the first few seconds and then decreased mid-way in the etch cycle due to strong F uptake. Future experiments will attempt to determine whether the observed decrease of the Si etching rate due to wall conditioning can be attributed to a reduction of the fluorine concentration during the etch cycle or to a higher density of fluorocarbon radicals during the passivation cycle.

5:00pm **PS1-WeA10 Spatially-resolved Optical Emissions Spectroscopy of Capacitively Coupled Discharges***, **G. Franz**, I. Krstev, F. Schamberger*, Hochschule München, Germany

Optical emission spectroscopy has evolved a mighty tool for evaluating the high-energy tail of the electron energy distribution function EEDF [1]. Since it is a non-evading technique, a spatially-resolved measurement cannot be performed, which limits its general applicability, especially for inhomogeneous plasmas, in particular capacitively-coupled discharges with their thick plasma sheaths and large rf electric fields, and microwave-driven plasmas which exhibit a very high plasma density in front of the microwave window which prevents the penetration of the microwave into deeper regions of the reactor. A spatially averaging technique therefore overdraws the region close to the window leading to erroneous results and conclusions.

To overcome these limitations, a cyclindrical parallel-plate reactor was equipped with a magnifying double lens system with different focal lengths halfway between the two “electrodes” to resolve radially dependent spectroscopic data obtained with the two actinometric gases Kr and Xe [2]. From these data, the electron temperature of the high-energy tail of the EEDF of capacitively coupled discharges through argon and the weakly electronegative gas mixture CF_4/O_2 can be calculated [3].

These data are modeled with ray tracing programs to evaluate the degree of magnification. Compared with an experimental setup with a plane window instead of a converging lens and only one focusing lens for the glass fiber, we can enhance the S/N ratio by a factor of at least 100 yielding a radial resolution of about 1 – 2 mm which is in the same range of Langmuir probes.

Compared with measurements obtained with Langmuir probes in the plasma bulk, electron temperatures show in fact the expected behaviour of definitely hotter temperatures.

[1] V.M. Donnelly, J. Phys. D: Appl. Phys. **37**, R217 (2004)

[2] G. Franz, I. Krstev, F. Schamberger, Plasma Sci. Techn. **14**(8), to be published 2012

[3] M.V. Malyshev and V.M. Donnelly, J. Vac. Sci. Technol. **A15**, 550 (1997)

5:20pm **PS1-WeA11 Model-based Ion Energy Control in ICP Etcher***, **M. Klick***, Plasmetrex, Germany*, H.P. Maucher*, United Monolithic Semiconductors

In particular for III-V semiconductors, plasma processes close to active zones of surface-sensitive devices are critical, demanding low damage through ion bombardment and so an excellent process understanding and control. In order to get the ion energy into the right range, the bias power is switched off working then a downstream-like mode. A complete model of the entire system with this special setup is presented and validated. It demonstrates that the bias matchbox capacitances are excellent control elements for the ion energy. We can also show that the Vp measurement is not representing the ion energy here. The ion energy is estimated by the sheath voltage from the model and shows a reasonable correlation to the etch rate observed.

This paper focuses on a general method to characterize equipment and plasma by a combination of off-line and real-time measurements. The first major goal of this paper is to show how reduced models of plasma equipment can be used to estimated important plasma parameters as to understand how the plasma process works. The equivalent circuit i only a tools to explain the over all plasma physical picture, it does mean that an equivalent circuit is always the right tool to describe a plasma. This resulting, reduced and so also not self-consistent model must be verified and then used for the ion energy control in an ICP etcher.

The model is based on an combined plasma and RF model in the special case of an existing bias matchbox but zero bias power. The control elements are the capacitance in the bias matchbox. We show the tune capacitance to be an excellent control element, but we can also demonstrate that – at least in this case – an RF peak voltage measurement is not representing the ion energy and alone not very useful.

Trikon/Aviza Omega 201 ICP etcher was used. A 100 mm electrode, a cylindrical coil around a ceramic chamber wall, and a Al chamber lid are main parts of the chamber.

Usually two generators are running at 13.56 MHz as master and slave with an adjustable phase shift between source and bias generator. In our case the bias generator is switched off in order to achieve a very low ion energy and thus almost no damage at the wafer. First investigations have shown that the position of load and tune capacitance in the bias matchbox to be very important for etch rate and wafer damage. Therefore a model was built to understand and finally to utilize these effects for process control.

5:40pm **PS1-WeA12 High Energy IED Measurements with MEMs based Si Grid Technology Inside a 300mm Si Wafer***, **M. Funk**, B.G. Lane, L. Chen, J. Zhao, R. Sundararajan,* Tokyo Electron America*, Y. Yamazawa*, Tokyo Electron Limited, Japan

The measurement of ion energy at the wafer surface at conditions that are realistic for commercial equipment and process development without extensive modification of the reactor geometry has been an industry challenge. High energy, wide frequency range, process gases tolerant, minimally perturbing, contamination free and accurate ion energy measurements are the base requirements. In this work we will report on the complete system developed to achieve the base requirements, including the safe and easy use by engineers. The system includes: a reusable silicon ion energy analyzer (IEA) wafer, signal feed through, RF confinement, and high voltage measurement and control.

The commercial manufacturing of an IEA system at a reasonable cost involves many disciplines, but can be achieved through the use of commercial methods and suppliers. Design aspects will be presented, including MEMs silicon etch technology that enables features in the sensor design that overcomes challenges in high voltage RF potentials while minimizing ion neutralization. The IEA wafer detail design required careful understanding of the relationships between the plasma Debye length, the number of grids, intergrid charge exchange (spacing), capacitive coupling, materials, and dielectric flash over constraints. RF confinement with measurement transparency was addressed so as not to disturb the chamber plasma, wafer sheath and DC self-bias as well as to achieve spectral accuracy. For commercial plasma etch reactors the wafer is floating at

several kV relative to the outside ground and often the plasma wetted DC ground area is small and not well defined. To overcome the difference between the wafer surface and the outside environment a non-perturbing measurement system was developed that can be isolated and floated by several thousands of volts, while making accurate ion energy current and voltage measurements.The experimental results reported were collected using a commercial parallel plate etcher powered by a dual frequency (VHF + LF) bottom electrode; with various power combinations. Various process gases were tested and variations by pressure were tested to confirm the robustness and sensitivity of the physical design and measurement circuit and methods.

Plasma Science and Technology
Room: 25 - Session PS2-WeA

Plasma Surface Interactions during PECVD and Plasma Surface Modification
Moderator: C.A. Wolden, Colorado School of Mines

2:00pm **PS2-WeA1 Surface Modifications Induced by Extreme Fluxes of Low-Energy Ions**, ***G. De Temmerman***, *K. Bystrov,* FOM Institute DIFFER, Netherlands, *M.J. Baldwin, R.P. Doerner,* University of California San Diego, *L. Marot,* University of Basel, Switzerland, *H.Y. Xu,* Tsinghua University, China, *M.C.M. van de Sanden*, FOM Institute DIFFER, Netherlands **INVITED**

The interaction of energetic particles with solid surfaces is at the core of numerous applications such as thin film deposition or materials processing. Ion-beam processing, for example, allows nanostructure formation on metal and semiconductor surfaces, while reactive ions can be used to chemically modify surfaces during nitriding for example. Those processes usually involve ions with energies above 100eV where ion-induced damage creation and physical sputtering are expected, and are relatively well documented. In a fusion reactor, at locations where the plasma intersects with the solid surfaces, plasma-facing surfaces are bombarded by extreme particle fluxes (up to $10^{24}m^{-2}s^{-1}$ or $1.6x10^{5}A.m^{-2}$), albeit with energies below 50eV. While the ion energy is below the damage threshold for the incoming ions, the particle flux is high enough to cause a local supersaturation of mobile gas particles within the implantation zone and strong surface morphology changes as a result of cluster/bubble growth.

Combining a high efficiency plasma source and a strong magnetic field, linear plasma devices (LPD) can generate such high ion fluxes and allow fundamental studies of plasma-induced surface modifications under high heat and particle fluxes. The effect of high fluxes of hydrogen, helium and neon ions on metal surfaces, such as tungsten, has been investigated over a wide range of surface temperatures (300-2000C) and ion energies (10-50eV). In all cases, the surface modifications depend strongly on these two parameters, which control the near-surface particle trapping and material properties (mechanical properties, self-diffusion).

Nanostructuring of the surface through formations of ripples or nanoscopic voids is observed for hydrogen irradiation. In the case of helium, a fibreform nanostructure is formed with a typical size in the range 20-1000nm depending on the surface temperature. For neon ions, both a fine-scale ripple structure and large blisters are observed on the surface.

An overview of these results will be given with an emphasis on the surface properties and the application of low-energy ion fluxes as a surface processing technique.

2:40pm **PS2-WeA3 Investigation of Plasma-Surface Interactions Between Hydrogen Radical and Chemically Amplified Photoresist**, ***A. Malinowski***, Institute of Electron Technology, Poland, *M. Sekine, M. Hori, K. Ishikawa, H. Kondo, T. Takeuchi, T. Suzuki,* Nagoya University, Japan, *A. Jakubowski, L. Lukasiak,* Warsaw University of Technology, Poland, *D. Tomaszewski*, Institute of Electron Technology, Poland

As FinFET transistors become necessary, FEOL etch processes will become much more challenging, bringing new constraints to etch selectivity, anisotropy, and etch damage. System-on-a-chip RF and analog devices may have double and triple gates and can be subjected to 12 or more photoresist (PR) removals. Thus development damage-less PR removal is critical for reducing plasma induced transistor electrical parameters fluctuations. In addition to poor uniformity or heavy environmental burden, hydrogen radical-based PR removal is expected to overcome critical problem of damage to the device inborn to currently used PR removal based on oxygen plasmas. As double and "multi" ArF 193nm patterning solutions continue to be a significant vehicle for extending Moore's Law, it is imperative to investigate plasma-surface interactions between hydrogen radical and chemically amplified ArF 193nm PR. The key element from point of view of etch reaction process kinetics investigation is radical sticking coefficient (SC).

In our study we have developed novel technique for radical SC estimation based on processing of PAPE structure (PAllet for Plasma Evaluation) followed by numerical simulation. Our approach is based on normalized profiles matching of etched PR thickness on parallel plate after PAPE structure processing, using hydrogen high density radical source, with simulated profile of number of stuck radicals on the same plate.

Understanding of the interactions of atomic hydrogen with ArF 193nm PR surface is of both fundamental and technological interest thus recombination mechanism of hydrogen atom on PR surface must be considered. In our approach SC is a sum of etch probability (EP) and recombination probability (RP) and estimated values of EP (0.07) and RP (0.1) reveal fact that recombination dominates during PR etching by hydrogen. Since recombination lowers the number of radicals that are bound to the surface, the reactive species coverage is reduced by this process. Dominance of recombination in conjunction with very low value of EP itself explains very low etch rate, which is on the order of a few nm per minute (it was 3.8 nm/min). In addition similarity of RP obtained in this study and Koleske et al. reveals that the recombination is the result of a gas phase atom abstracting an atom of the same type that has previously chemisorbed to the surface according to the Eley-Rideal mechanism.

Inefficiency of the kinetic energy loss by hydrogen radicals during the PR surface collision, by means of phonon excitation or momentum transfer explains very low value of EP (0.07). Increase of temperature (323 K) of the structure involved proportional increase of EP (0.09).

3:00pm **PS2-WeA4 Kinetic Theory of the Sheath near Electron Emitting Surfaces**, ***J.P. Sheehan***, University of Wisconsin Madison, *I.D. Kaganovich,* Princeton Plasma Physics Laboratory, *N. Hershkowitz,* University of Wisconsin Madison, *Y. Raitses*, Princeton Plasma Physics Laboratory

It has long been known that electron emission from a surface significantly affects the sheath surrounding that surface. Typical fluid theory of a planar sheath with emitted electrons assumes that the plasma electrons follow the Boltzmann relation and the emitted electrons have zero energy at the surface and predicts a potential drop of 1.03 T_e across the sheath when the surface is allowed to float. By removing the assumption that all plasma electrons entering the sheath are reflected back into the bulk plasma (i.e. the Boltzmann relation) and considering those electrons lost to the wall, the predicted sheath potential is reduced to 0.91 T_e. Analysis of this type has been published by various authors, but our work presents a more accurate model. We performed an analytical study of sheath and presheath structure making use of a kinetic description of the emitted and plasma electron densities in the self-consistent electric field. It is shown that kinetic theory predicts that the sheath potential depends on the ratio of temperatures of plasma and emitted electrons (Θ_e). For $\Theta_e = 5$ (for example, for 0.2 eV emitted electron temperature and 1.0 eV plasma electron temperature), theory predicts a sheath potential of half that predicted by fluid theory. The effects of a bi-Maxwellian Electron Energy Distribution Function (EEDF) were considered. These predictions were compared to measurements made in a non-magnetized plasma confined by a multidipole chamber which has a bi-Maxwellian EEDF. A barium-tungsten dispenser cathode was used as a planar emitted electron source. The inflection point in the limit of zero emission emissive probe technique was used to measure the plasma potential in the sheath and presheath near the emitting surface. These results were compared to the kinetic theory and the effects of the bi-Maxwellian EEDF were taken into account.

4:00pm **PS2-WeA7 Probing CF and CF_2 Surface Reactivities in Inductively-Coupled Fluorocarbon Plasmas**, ***M.F. Cuddy****, *E.R. Fisher*, Colorado State University

Inductively-coupled fluorocarbon plasmas (FCPs) provide a wide range of potential applications from circuitry fabrication to preparation of optical coatings. In these systems, etching and deposition processes often occur simultaneously, with the net effect of surface processing dictated by the balance between the two phenomena. The behavior of CF_x (x=1,2) species in particular provide insight into these competing processes and allow for elucidation of the mechanisms of FCP processing. We have examined CF_x radical scatter coefficients (*S*) at the gas-surface interface for a range of FCPs during plasma-enhanced chemical vapor deposition (PECVD). Our imaging of radicals interacting with surfaces (IRIS) experiments reveal that CF and CF_2 species scatter from surfaces with a high probability in each of the systems investigated. These high scatter values are related to the ion energies of nascent plasma species, as measured by mass spectrometry. Highly energetic ions ablate fluorocarbon passivation layers to extricate CF_x

* Coburn & Winters Student Award Finalist

units. The presence of vibrationally hot $CF(^2\Delta)$ radicals correlates directly with increasing scatter values for $CF(^2\Pi)$, suggesting that internal energy transfer at surfaces is another important factor contributing to the observed *S*. The connection between interfacial interactions and the PECVD-deposited film is a critical component to consider for improved plasma applications and for designing specificity in fluorocarbon film properties. Ultimately, by controlling the parameters associated with our plasma systems, we can create tailored films with specific compositions and surface energies. The efforts recounted here offer additional insight into the fundamental plasma processes so crucial for advancement of plasma technology.

4:20pm **PS2-WeA8 Effects of Ar Ion Bombardment on Protection of Organosilicate Glass from O_2 Plasma Damage**, ***H.Ur. Kazi***, *S. Gaddam, J.A. Kelber*, University of North Texas

In-situ XPS studies of Ar ion bombardment on organosilicate glass (OSG) films at ion kinetic energies between 500eV and 900eV demonstrate that such bombardment inhibits O2 plasma-induced carbon loss by forming an SiO2-like overlayer, and that the degree of protection correlates directly with increased ion energies, but not the thickness of SiO2 overlayer. Bombardment at 500eV results in a ~3 Å thick SiO2overlayer and subsequent O2 plasma treatment results in a slower rate of carbon loss from the surface region than observed for a vicinal film, but complete carbon removal is observed after 3 min O2plasma treatment under these conditions. In contrast, bombardment by a similar flux of 900eV ions results in a SiO2-like overlayer of similar average thickness, but with greatly inhibited rate of carbon loss upon subsequent O2 plasma exposure. Ar ion bombardment (900eV) in the presence of NH3 (1 x 10-6 Torr) results exclusively in Si-N rather than C-N bond formation, and dramatically increases the average thickness of the Si-O-N overlayer to 22 Å. The formation of this overlayer further reduces the rate of subsequent O2 plasma-induced carbon loss compared to 900eV Ar ions alone. These results indicate Ar ion bombardment causes Si-C bond scission. Subsequent NH3 reaction results in Si-N bond formation and inhibits Si-Si and Si-O-Si formation, increasing the thickness of the ion-induced damage overlayer. The data indicate that ion kinetic energies are a critical parameter in protective noble gas plasma treatments to inhibit O2 plasma damage, and also indicate that high energy ions alone can provide better protection against carbon loss when compared to plasmas or VUV photons.

Acknowledgement: This work was supported by the Semiconductor Research Corporation under Task ID 2071.002. The authors thank Novellus Systems Inc. for providing the low k samples. David Graves and Joe Lee are also acknowledged for stimulating discussions.

4:40pm **PS2-WeA9 Ion-Surface Interaction during Microcrystalline Silicon Thin Film Growth**, ***J. Palmans***, *A.C. Bronneberg, X. Kang, M.C.M. van de Sanden, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, the Netherlands

Thin-film silicon solar cells extensively use hydrogenated microcrystalline silicon (μc-Si:H) where large area and fast deposition processes are considered key issues. Both requirements can be fulfilled when operating in the so-called high pressure depletion (HPD) regime in a parallel plate capacitively coupled plasma (CCP). This latter involves high plasma powers (~0.5 W/cm^2), enabling high growth rates through high silane (SiH_4) depletion, and high pressures (> 0.75 Torr) enhancing the material properties by suppressing the ion bombardment. In this work direct ion measurements obtained in a parallel plate CCP are presented for two collisional pressure regimes enabling a quantitative comparison of the role of ions during the plasma-surface interaction and its relation to the amorphous-to-microcrystalline silicon phase transition as determined in both the HPD (10.50 Torr) and a low pressure (0.45 Torr) regime by varying the SiH_4 flow rate, while preserving hydrogen (H_2) flow rate and power density. By relating Raman and infrared absorption spectroscopy data the absence of the narrow high stretching modes and oxidation processes for the solar-grade μc-Si:H thin films has been demonstrated. Next to material analysis, this contribution will address selected aspects of plasma-surface interaction during μc-Si:H deposition. A capacitive probe has been implemented to study the ion flux for a range of parameters, i.e. silane flow rate and plasma power, whereas ion energies are determined with a retarding field energy analyzer (limited to pressures < 0.75 Torr), both implemented in the substrate holder. In the HPD regime an increase of SiH_4 flow rate (0-10 sccm) is found to induce only a moderate increase in ion flux, accounting for 30% of the growth flux for solar-grade material [1]. With ion energies limited to below 19 eV (in collisionless H_2 plasma), less than 6 eV are estimated to be available per deposited Si atom, suggesting that we are either in a regime of Si surface atom displacement, or more likely that a thermal spike is induced at the surface by the arrival of ions, enhancing the radical surface diffusion. Since the ion energy measurements are compatible only with low pressure, this study supports the direct correlation between material quality and plasma-surface interaction in terms of ion energy. The novel insights obtained can lead to the further development of deposition techniques in order to meet the stringent requirements of solar cells in terms of efficiency and production costs.

[1] A.C. Bronneberg, X. Kang, J. Palmans, P.H.J. Janssen, T. Lorne, M.C.M. van de Sanden and M. Creatore,

Submitted to J. Appl. Phys. (2012)

5:00pm **PS2-WeA10 Time Resolved Characterization of Pulsed ICP CH_4 – H_2 Based Plasmas**, *S. Jacq,* ***L. Le Brizoual****, C. Cardinaud, A. Granier*, University of Nantes - CNRS, France

Pulsed rf plasmas are increasingly being employed for plasma etching or deposition. In the case of etching, as the semiconductor feature sizes decreases and feature density increases, the industry is facing the increasing challenge of finding new plasma processes for the requirement of the next devices generation. CH_4-H_2 based plasmas are widely used for dry etching of II-VI and III-V semiconductors. Pulsed plasmas combined to time resolved measurements are known to be powerful tools to study species kinetics. In this study, pulsed CH_4-H_2 plasmas created in a low pressure inductively coupled rf plasma (ICP) are analyzed by time resolved optical emission spectroscopy (TR-OES), mass spectrometry (TR-MS) and electrostatic probe measurements. Plasma conditions are the following: 800 or 1000 W RF power, 20 mTorr pressure, 5 to 50 ms period and 10 to 50 %duty cycle. A cylindrical Langmuir probe and a planar probe are used to measure the electron density (n_e), electron temperature (T_e) and ion flux density. The species creation kinetics is investigated by TR-OES. Since no emission occurs during the off time (n_e and T_e decreases drastically), the double pulse technique is used with a probing pulse time of 0.75 ms. This communication is focused on pseudo-actinometry for the kinetics of H atoms and radicals (CH..). Mass spectrometry is carried out with a time resolved and energy-resolved mass spectrometer on CH_3. For TR-MS, the transit times in the apparatus are calculated for each ion.

During the post-discharge, the decay characteristic time is below 1 ms for H atom density. The time evolution of ne over one period reveals that ne needs 1 ms to reach a stationary state and decreases with a characteristic time of about 0.1 ms. However, the decrease time of Te seems to be shorter than 0.1 ms. Although the H atom kinetics is very fast, and characterized by a decay time below 1 ms, it is slower than the time evolution of n_e and T_e. However, considering the diffusion coefficient of H atoms in the various gas mixtures, different rise and decrease characteristic times could indicate different reaction probabilities on the walls, in relation with the gas mixture. Characteristic times and associated reaction probabilities, using Chantry's formalism are determined to be equal to 0.52 ms (on time) 0.80 ms (off time) which corresponds to H loss probability γ_{on}=0.3 and γ_{off}=0.1. Similar mass spectrometry measurement on CH3 plasma species will be presented. Influence of ion bombardment on the H loss rate at the chamber walls is discussed and this seems to be the key point for chamber conditioning in the pulsed mode.

5:20pm **PS2-WeA11 Plasma-Surface Interactions, Erosion, and Impact on Plasma Distribution Functions**, ***N. Fox-Lyon***, University of Maryland, College Park, *D.B. Graves,* University of California Berkeley, *S.Y. Moon, V.M. Donnelly, D.J. Economou,* University of Houston, *G.S. Oehrlein*, University of Maryland, College Park

Plasma-surface interactions can play a large role in changing characteristic plasma distribution functions. To improve our fundamental understanding of these effects, we leverage several plasma characterization techniques (Langmuir probe, ion energy/mass analyzer, optical emission spectroscopy) with real-time characterization by *in situ* ellipsometry of the eroding plasma-facing surface. Using these methods, we qualitatively and quantitatively studied the time evolution of gaseous and surface derived plasma impurities. High-density inert plasmas (Ar) and low-density reactive plasmas (H_2, D_2) respond differently to molecular impurities in the plasma. When H_2/D_2 or surface/gaseous derived CH_X -related impurities are introduced into Ar plasma, large changes in plasma properties are observed. We report on changes to the ion energy/mass distributions, electron temperature/distribution functions, and plasma density for different conditions . CH_X effects on H_2 and D_2 plasmas, and H_2/D_2 plasma mixtures were also investigated. We also explore the effects of changing the relative C:H fluxes into the plasma from eroding surfaces using graphitic (high C:H ratio) and polymeric (lower C:H ratio) films. In steady-state contact with plasmas, hydrocarbons are eroded as C, H, and CH_X impurities into the plasma reflective of their initial C:H ratios. Along with these studies, we have compared how varying the gap distance between the plasma generation coil and hydrocarbon substrate electrode affects impurity fluxes and plasma properties. A comparison of plasma properties for two different inductively coupled plasma reactors has also been completed and sheds light on how plasma properties and observed trends change for different geometries and plasma sources.

5:40pm **PS2-WeA12 MD Simulations of Hydrogen Plasma Interaction with Graphene Surfaces**, ***E. Despiau-Pujo***, *A. Davydova, G. Cunge,* CNRS/UJF-Grenoble1/CEA LTM, France, *L. Magaud,* CNRS/UJF Institut Neel, France, *D.B. Graves*, University of California Berkeley

Due to its unique 2D structure and its outstanding physical, chemical and mechanical properties, graphene is a promising candidate for a large number of novel applications in microelectronics, for transparent conducting electrodes, sensors or energy storage devices. The successful development of graphene-based technologies relies on the capability to grow and integrate this new material into sophisticated devices but the nm-scale control of graphene processing overwhelms current based-plasma technology. Therefore, innovative technological steps have to be developed to allow the growth of graphene layers on large areas wafers and their patterning using conventional lithography and plasma etching schemes.

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous-wave plasma processes are not able to selectively etch ultrathin films without damaging the active layers of nanoelectronic devices. In order to achieve uniform/smooth patterning, doping or chemical modification of graphene films without damaging the substrates, one possible alternative is to use pulsed-plasma discharges which exhibit lower average ion energies (thus minimizing surface damage) and are promising to achieve sub-nm thick layers etching. However, the interactions between reactive pulsed plasmas and surfaces are so complex that the efficient development of new processes requires numerical simulations. Therefore, we propose to develop Molecular Dynamics (MD) simulations to understand the role of ion energy in plasma-graphene interaction and to determine the relationship between the flux/energy of reactive species (ions, radicals) bombarding the surface and its structural/chemical modifications.

In this paper, we investigate the interaction between hydrogen plasma species and single/multilayer graphene samples via MD simulations. C-H interatomic potential curves and associated energy barriers are reported depending on the H impact position (top, bridge, hollow or edge sites of GNRs). The influence of graphene temperature and incident species energy on adsorption, reflection and penetration mechanisms is presented. Except for impacts at GNRs edges or at defects location, H species are shown to experience a repulsive force due to delocalized π-electrons which prevents any species with less than ~ 0.7eV to adsorb on the graphene surface. It also appears that the chemical binding of H to sp2-C requires a local rehybridization from sp2 to sp3 resulting in structural changes of the graphene sample. H^+ bombardment of ABA- and ABC-stacked multilayer graphene sheets are compared and the possibility to store hydrogen between consecutive layers is discussed.

Plasma Science and Technology
Room: 24 - Session PS1-ThM

Plasma Processing for Disruptive Technologies (NVM, TSV, etc.)
Moderator: S. Hamaguchi, Osaka University, Japan

8:20am **PS1-ThM2 Damage Free Cryogenic Etching of Porous Organosilica Ultralow-k Film**, ***L. Zhang***, IMEC, Belgium, *R. Ljazouli, T. Tillocher, P. Lefaucheux, R. Dussart,* GREMI CNRS/Université d'Orléans, France, *Y. Mankelevich,* Moscow State University, Russia, *J.-F. de Marneffe, S. de Gendt, M.R. Baklanov*, IMEC, Belgium

Porous organosilicates (OSG) are popular candidates as low dielectric constant materials for interconnect application. However, the integration of this class of materials remains challenging, especially for k≤ 2.3 materials with a large open porosity. Due to carbon depletion and surface modification, porous low-k materials suffer from plasma induced damage (PID) that leads to k value degradation and high leakage current. In this paper, we report a cryogenic low-k etching approach that benefits from a sidewall surface protection effect. It is known that, at cryogenic temperature, an SiO_xF_y passivation layer forms more easily on the surface of the material being etched, providing efficient sidewall protection.In this work, cryogenic etching is applied to porous organosilicate ultralow-k materials with k=2.3 and k=2.0, which are prepared by Spin-coating and PECVD methods respectively. Influence of the chuck temperature and bias power with different plasma chemistries has been investigated in an ICP chamber. Plasma induced damage is evaluated by means of spectroscopic ellipsometry (SE), Fourier-transformed infra-red spectroscopy (FTIR) and time of flight secondary ion mass spectroscopy (TOF-SIMS). Blanket low-k films are exposed to pure SF_6 plasma with different chuck temperatures, ranging from 20°C to -120° C. Almost no carbon depletion is observed when the chuck temperature is below a threshold point (-70°C and-120°C for k=2.3 and k=2.0 materials respectively). By addition of SiF_4 and O_2 to the gas discharge, etching rate is reduced as a result of enhanced SiO_xF_y polymerization. In order to evaluate the damage depth, an equivalent damage layer (EDL) is calculated based on the measurement of FTIR methyl group loss. The EDL decreases by increasing the proportion of SiF_4/O_2 in gas discharge, which confirms the protection effect of the SiO_xF_y passivation layer. In addition, the formation of alkyl alcohol polymer during cryogenic etching is observed from ex-situ FTIR, which is a major etch by-product at cryogenic temperature due to the lack of activation energy for complete oxidation of the methyl groups into CO_2 and H_2O. Our experiments also show that this polymer can be easily removed by high temperature anneal without additional damage to low-k film. This incomplete oxidation of Carbon-based etch reaction products reveals the mechanism for reduced Carbon depletion during cryogenic etching. A protection model is proposed, for porous SOG etching at cryogenic temperature, based on SiO_xF_y growth and incomplete oxidation. Although the etch by-products cannot plug the interconnected pores, they condense on their surface and retard the oxidation of methyl groups.

8:40am **PS1-ThM3 Deep GaN Etching : Role of $SiCl_4$ in Plasma Chemistry**, ***J. Ladroue,*** GREMI - STMicroelectronics, France, *M. Boufnichel,* STMicroelectronics, France, *T. Tillocher, P. Lefaucheux, P. Ranson, R. Dussart*, GREMI - Polytech Orleans/CNRS, France

Gallium nitride (GaN) is currently used for light emitter devices due to a large and direct bandgap. Otherwise, GaN physical properties open new prospects in microelectronics manufacturing. By combining a wide bandgap (3.4 eV), strong chemical bonds and a high electron mobility, GaN based devices should operate under higher temperature, higher power and higher frequency than typical silicon devices.

It was shown that wet etching is limited due to inert chemical nature of GaN [1], especially in the c-plan where the etching is generally needed [2]. Therefore, plasma etching is essentially used due to the combination of chemical and physical effects. Chlorine plasmas are used because $GaCl_3$ is the most volatile Ga etching product.

Due to the power density applied to the next generation of power devices, an etched depth as high as 6 to 10 µm is typically required. This could be qualified as deep GaN etching compared to the etched depth needed for light emitter devices which are of the order of few hundreds nanometers.

It was shown that bottom surface defects are linked with dislocations and nanopipes created during the epitaxial growth of GaN [3]. We will show that etched surface presents either pits or columnar defects closely linked with plasma conditions. Mass spectrometry data confirms the importance of ClO species in columnar regimes. We will show that $SiCl_4$ is able to scavenge ClO and allows to provide a smoother surface. $SiCl_4$ can be added in plasma gas or as the etching product of a silicon coverplate. We will also present data showing the influence of $SiCl_x$ passivation layer on SiO_2 hard mask selectivity. Plasma diagnoscics such as optical emission spectroscopy or mass spectrometry will allow us to propose mechanism of formation of this passivation layer.

[1] D. Zhuang and J.H. Edgar, Mat. Sci. and Eng., 48 (2005) 1–46

[2] D. A. Stocker, E. F. Schubert, and J. M. Redwing. Applied Physics Letters, 73 (1998) 2654–2656

[3] J. Ladroue, A. Meritan, M. Boufnichel,P. Lefaucheux, P. Ranson, and R. Dussart, J. Vac. Sci. Technol. A 28, (2010) 1226

9:20am **PS1-ThM5 Etching Reaction Analysis of CoFeB by Carbon Monoxide / Methyl Alcohol Based Plasmas**, ***K. Karahashi****, T. Ito, S. Hamaguchi*, Osaka University, Japan

Magneticrandom access memory (MRAM)devices,which are composed of magnetic-tunnel-junction (MTJ) stacks, have potential to replace static random access memory, dynamic access memory, and flash memory devices because they can provide high speed operation, low operating voltage, and nonvolatile storage. For the realization of high-density MRAM devices, dry etching of magnetic thin films must be developed.Argon ion milling seems to be almost the only etching technique available in the current manufacturing processes for MRAM devices. However, capabilities of Argonion milling for anisotropic and selective etching of magnetic films are severely limited and therefore new technologies of reactive ion etching (RIE) for magnetic films are now seriously sought.RIE processes based on CO/NH3 and CH3OH are candidates for selective etching processes of magnetic thin films. In this study, we have focused on etching processes of CoFeB alloy thin films and examined etching reactionscaused by energetic CO+ or O+ ions, which are considered to be the major etchants of CO/NH3 or CH3OH plasmas. We have determined the etching yields and analyzed surface reactions, using a mass-selected ion beam system. The ion beam system is designed to inject mono-energetic single-species ions into a sample surface in ultra-high vacuum conditions. The reaction chamber is equipped with an X-ray photoelectron spectroscopy (XPS) for in-situ chemical analyses of irradiated surfaces. The ion beam energy used in this study is in the range of 300-1000eV. The etching rates are determined from measured depth profiles of irradiated surfaces and ion fluxes. It has been found that the etching rates of CoFeB by Ar+ ions are smaller than those of CoFe. Thereforephysical sputtering yields of such magnetic thin films are affected byboron atoms contained in them.The etching rates of CoFeB by CO+ ions are found to belower than those by Ar+and increasewiththe cobalt content. From XPS analysis ofCO+ irradiated CoFeB surfaces, it has been found that, although cobalt does not oxidize,iron of CoFeBoxidizes and inhibits the etching reactions. Therefore, the etching rates of CoFeB by CO+ irradiation are dependent on the atomic compositions of CoFeB films. The results suggest that design of the atomic composition of CoFeBfilms is important also for the etching process development.This work was supported by the Semiconductor Technology Academic Research Center (STARC).

9:40am **PS1-ThM6 The Etching Characteristics of Flexible Substrate in Inductively Coupled Plasma System for Flexible Electronics**, ***Y.S. Chun****, Y.H. Joo, C.I. Kim*, Chung-Ang University, Republic of Korea

Recently, many attention was given to the flexible electronics due to its future applications, such as flexible display and e-paper, etc. In order to fabricate the devices on the flexible substrate, such as PES, PAR, and PI, the etching characteristics of the substrate should be studied respect to other deposited thin film layers because the surface roughness and etch by-products could affect the device performance. Also, the devices can be embedded in the flexible substrate, where the flexible substrate should be etched away.

In this study, polyarylate (PAR) and polyethersulfone (PES) flexible substrates were etched by using inductively coupled plasma (ICP) system at room temperature. BCl_3, CF_4, and Ar mixed chemistry gases were used to achieve a high etch rate and good selectivity respect to the other metal (Al) or oxide (ZnO) layers. The etching charactersits of the flexible susbstrate were studied by varying the process parameters, including process pressure, DC bias voltage, RF power, and gas mixing ratio. In addition to the etch rate and selectivity, the surface chemical bonding structure and roughness were studied because they are the important factors for the device fabrication and performance.

The etch rate and selectivty were measured by using a depth profiler (alpha-step 500, KLA tencor) and the surface roughness was measured by atomic force microscopy (AFM). The chemical states of etched surfaces were

investigated with X-ray photoelectron spectroscopy (XPS). The elemental analysis of etched surfaces was investigated with the auger electron spectroscopy (AES) analysis.

10:40am **PS1-ThM9 Plasma Process Developments for Spintronics Devices**, ***K. Kinoshita***, Tohoku University, Japan **INVITED**

Demands for zero-standby-power systems have increased in order to realize low-carbon society. For this purpose, non-volatile spintronics devices which use magnetic tunnel junction (MTJ) are receiving much attention due to its endurance and high speed. Another important advantage of the spintronics devices is their compatibility to CMOS process. Up to now, 16 Mb MRAM has been in the market. And, developments are ongoing on 300 mm wafer of 90 nm CMOS node or beyond targeting Gb class memory capacity. To combine with the BEOL process, low temperature (<350 degree C) processes are required for additional processes to fabricate the MTJ cell. Use of plasma which enables low temperature process matches the needs.

Whether the target is memory or logic, following three plasma processes are the key to realize the spintronics devices: (a) Damage-less PVD of thin-film multilayered-stack materials. (b) Dry etch for magnetic multilayer stack materials. (c) Protective film CVD over MTJ cell. Multi-target magnetron-PVD is the key equipment to deposit uniform, ultra-thin, multi-stacked MTJ. MgO barrier film quality determined the performances of the MTJ [1]. An Ar milling process has long been used to etch magnetic materials. C-O(X)-based chemistry is increasing attracting attention recently due to its high etch selectivity between hard mask Ta and magnetic materials [2]. Here, degradation of device performances by chemical modification of magnetic materials is one of the issues. Recovery treatment becomes important for the next step [3, 4]. Process chemistry of the protective film CVD should not degrade materials used in MTJ. In addition, high enough quality is needed to protect the MTJ cell during the following BEOL processes [5].

All the unit processes should be evaluated by the MTJ performances after fabricating MTJ in a BEOL structure. In addition, total coordination of BEOL process including these MTJ fabrication processes is required.

This work was supported by JSPS through its FIRST Program.

[1] K. Ono et al., Jpn. J. Appl. Phys. 50, 023001 (2011). [2] I. Nakatani, IEEE Trans. Magn. 32, 4448 (1996). [3] K. Kinoshita et al., Jpn. J. Appl. Phys. 49, 08JB02 (2010). [4] K. Kinoshita et al., to be published on Jpn. J. Appl. Phys. 51, (2012). [5] K. Suemitsu et al., Jpn. J. Appl. Phys. 47, 2714 (2008).

11:20am **PS1-ThM11 Predictions of the Etch Behavior of Complex Oxide Films for High-k and Multiferroic Applications**, ***N. Marchack***, *J. Chen, J.P. Chang*, University of California at Los Angeles

The ongoing quest to improve the performance of integrated circuit devices has led to a burgeoning body of research in synthesizing multifunctional materials. However, these materials are often intrinsically etch resistant and thus ensuring high-fidelity patterning via plasma etching faces significant challenges. This study aims to demonstrate predictive capability for the etch behavior of novel materials, e.g. complex oxides, by combining an established phenomenological model with thermodynamics-based volatility diagram analysis. The material systems studied were the potential high-k dielectric HfxLayOz, and the multiferroic candidates YxMnyOz and BixFeyOz.

Experiments to validate the theoretical analysis were conducted an inductively coupled plasma (ICP) reactor equipped with a quadrupole mass spectrometer (QMS) for analyzing etch products and a quartz crystal microbalance (QCM) for measuring the etch rate *in situ*. The use of the QCM eliminated the need to subject the samples to unwanted reactions in atmosphere prior to etch rate measurement, and also allowed for materials that were unable to be analyzed by other methods such as spectroscopic ellipsometry. The reactor was also connected to a UHV transfer tube which allowed the surface composition to be studied via x-ray photoelectron spectroscopy (XPS) without exposure to ambient conditions.

The calculated etch rates of the HfxLayOz films in a 400W, 5 mT, Cl2 plasma varied from 8.3 to 181.9 Å/min (for -25V to -200V bias voltage, respectively), generally lower than that of pure HfO2etched in comparable conditions by ~16 to 31%. The maximum etch rate observed for a 400W, 15mT BCl3condition was 61 Å/min (at -175V), with net deposition (1.34 – 4.71 Å/min) observed below -75V bias voltage. QMS was used to characterize the etch products, with LaCl, LaO3, LaOCl and LaO2Cl (3.4 : 4.0 : 3.1 : 1.0) and LaB, LaB2O, LaBOCl and LaO2Cl (1.2 : 1.1 : 1.3 : 1.0) observed as the dominant La-containing species in Cl2 and BCl3conditions, respectively. The surface compositions of the films post-etching revealed a decrease in the La and Hf fractions after Cl2 and BCl3exposure, with a more significant reduction in La compared Hf (~50% v. ~19%) as determined via XPS. Similar analysis for the multiferroic oxides will be presented and comparative etch behavior analyzed through the aforementioned theoretical framework.

11:40am **PS1-ThM12 Sub-30nm Pitch Patterning of FEOL Materials for Aggressively Scaled CMOS Devices for 10 nm Node and Beyond**, ***H. Miyazoe***, *S. Engelmann, H. Tsai, M. Brink, B.N. To,* IBM T.J. Watson Research Center, *J. Cheng, C. Liu,* IBM Research - Almaden, *W.S. Graham, E.M. Sikorski, M.A. Guillorn, N.C.M. Fuller, E.A. Joseph*, IBM T.J. Watson Research Center

As the feature size in CMOS technology continues to shrink, patterning below 40 nm pitch faces many challenges. Continued delays in production worthy EUV lithography has driven an interest in directed self-assembly (DSA) [1] and sidewall image transfer (SIT) [2] patterning. Both techniques can augment conventional lithographic patterning by providing sublithographic multiplication of feature pitch. In this work, we leverage the results of a parametric study of factors impacting fine feature patterning [3] to further optimize DSA and SIT based patterning in the sub 30 nm pitch regime. Recently, we successfully demonstrated the transfer of "fingerprint" DSA patterns to the materials typically used in front end of line (FEOL) processing. Patterning of Si, SiN_x and SiO_x at a ~28 nm feature pitch using poly(styrene-block-methyl methacrylate) (PS-b-PMMA) block copolymers was shown [4]. In this work, we discuss further optimization of the etch processes used to pattern the organic underlayer in the masking material stack as well as the substrate material. The use of templated DSA to generate line-space structures in the aforementioned materials was used to investigate the control of critical dimension (CD), line edge roughness and line width roughness throughout the patterning process. SIT-based patterning using metal oxide or nitride films as the side-wall hard mask was used to generate patterns in FEOL materials down to ~25 nm pitch. Typically, the CD of end lines are larger than the target CD of nested lines in structures generated by SIT. Dense/iso loading-like effects and other mechanisms to explain this phenomenon are explored. These initial patterning studies may play an important role in understanding feature formation and density limiting ground rules in future technology nodes. This work is sponsored by the DARPA GRATE (Gratings of Regular Arrays and Trim Exposures) program under Air Force Research Laboratory (AFRL) contract FA8650-10-C-7038.

[1] J. Cheng *et al.*, SPIE 2010. [2] H. Yaegashi *et al.*, SPIE 2012. [3] H. Miyazoe *et al.,* AVS2011. [4] S. Engelmann *et al.*, SPIE 2012.

Plasma Science and Technology
Room: 25 - Session PS2-ThM

Low Damage Processing
Moderator: E.A. Joseph, IBM T.J. Watson Research Center

8:00am **PS2-ThM1 New Approaches for Overcoming Current Issues of Plasma Sputtering Process during Organic Based Micro-Electronic Device Fabrication : Room Temperature & Plasma Damage Free**, ***M. Hong***, Korea University **INVITED**

While direct deposition of metal oxide thin films including transparent conductive oxide (TCO) and amorphous oxide semiconductor (AOS) on the organic layers, plasma damages against the organic materials are serious issues. These damages are believed to be mainly originated from highly energetic particles during the plasma sputtering process such as negative oxygen ions & reflecting neutrals from the target surface, etc. During the DC magnetron sputtering (DMS) process, most of energetic particles contribute in self-supplying of activation & crystallization energy and forming higher quality TCO thin film without an additional heating or post-annealing. However, the excessively accelerated negative oxygen ions can lead to fatal physical bombardment damages and defects in the oxide thin film, which are hardly recovered without post thermal annealing. To simply salve the inherent limitation of the DMS process, we are developing novel approaches for selectively filtering the negative ions by magnetic field arrays, named as Magnetic Field Shielded Sputtering (MFSS) process. The MFSS process effectively eliminates or suppresses the defect generation induced by the negative oxygen ion bombardments. The electro-optical properties of ITO thin films by the MFSS were superior to those by the conventional DMS at room temperature. While the DMS processed a-IGZO TFTs need a high temperature post annealing up to 400℃ for healing the internal defects in the AOS thin film, the MFSS processed a-IGZO TFT scarcely requires the post thermal annealing and shows very comparable electrical performance to the DMS processed one with a high temperature post annealing. To completely overcome the plasma related damage issues, we are developing the Neutral Beam Assisted Sputtering (NBAS) process; electro-optical properties of the ITO thin film by the NBAS were achieved

in lower resistivity (< 4.0×10−4 Ω·cm) and higher transmittance (> 90 % at 550 nm) with nano-crystalline structure at room temperature process. Furthermore, for a TCO top anode on the inverted structure OLED cell, the NBAS TCO deposition process has induced almost no damages on the underlying organic layers. On the other hand, gas barrier coatings are essential to prevent the permeation of water and oxygen for a high efficiency flexible AMOLED device. Key factors for formation of the high quality inorganic gas barrier to satisfy the extremely lower water vapor transition rate (WVTR) requirement for OLED cells (<1×10-6 g/m2/day) are suppression of nano-sized defect sites and gas diffusion pathways among the grain boundaries. To achieve the nano-sized defect free inorganic gas barrier layer, new nano-structured Al2O3 single gas barrier layer is developing by using the NBAS technology; current WVTR of the NBAS processed Al2O3 gas barrier films was as low as 5×10-6 g/m2/day by just single layer.

8:40am **PS2-ThM3 Novel Inward Plasma Etching System for Failure Analysis in Nano-Scale Semiconductor Devices**, ***T. Shimizu***, *T. Horie, Y. Naitoh,* AIST, Japan, *S. Takahashi, C. Iwase, Y. Shirayama, S. Yokosuka, K. Kashimura, S. Shimbori, H. Tokumoto*, Sanyu Co. Ltd., Japan

In a plasma system with a capillary-discharge tube, Yoshiki has demonstrated that the plasma can expand even along an upper gas-stream side of the tube under proper conditions (gas pressure, electric power, etc), even if the plasma is excited in the tube center. By utilizing this fact, we have developed an "inward" plasma etching (IPE) system, where the etching sample is set close to the tube end, and successfully applied to expose the metal wires for failure analysis of nano-scale semiconductor devices. Insulating oxide layers in a multi-layered semiconductor device was etched locally, cleanly and well controlled with process gas CF_4 . Thin metal wires about 90nm width embedded in the oxides were exposed without any damages (breaking, lifting off, etc) in much shorter time compared with the focused ion beam etching. Further, almost all etching products which flowed though the capillary tube were effectively analyzed with a quadrupole mass spectrometer. In a case of CF_4 gas etching of silicon wafer with thermal-oxides of about 600nm thick, mass peaks corresponding to SiF^+, SiF_2^+ and SiF_3^+ were detected and the intensity of SiF_3^+ was changed clearly at the boundary of silicon oxide and substrate silicon, indicating a good measure of the end-point detection. At the presentation, we shall present details of the system and its application.

9:00am **PS2-ThM4 Effect of Open Area Ratio and Pattern Structure on Fluctuations in Critical Dimension and Si Recess**, ***N. Kuboi***, *T. Tatsumi, M. Fukasawa, J. Komachi, T. Kinoshita, H. Ansai, H. Miwa*, Sony Corporation, Japan

The Si recess, which is caused after post-wet treatment in the Si gate etching process, can have a big effect on transistor properties such as threshold voltage (V_{th}) and off-state leakage current (I_{off}). We previously studied what caused the Si recess [1] and found through our analysis of a molecular dynamics (MD) calculation and a beam experiment that it could be the oxidation enhanced diffusion induced by incident hydrogen during HBr/O_2 gate etching [2]. The fluctuation in the Si recess depth (Δd_R) as well as in the critical dimension (ΔCD) is one of the key factors causing fluctuations in V_{th} (ΔV_{th}) and I_{off} (ΔI_{off}). The pattern dependence of the incident particle flux is related to Δd_R, therefore a prediction technology that considers this dependence is necessary in order to understand the effects on ΔV_{th} and ΔI_{off}.

To model the dependence, we assumed that three factors–mask open area ratio at the wafer level (global), chip level (semi-local), and local level (local)–affect ΔCD and Δd_R. We performed experiments using a dual frequency capacitively coupled plasma system. We used wafers ranging from 60 to 91 % (the global range (R_G) and the semi-local (R_S)) with various patterns of the photo-resist mask on the Poly-Si film. These samples were treated by the HBr/O_2 process under a pressure of 30 mTorr.

We found that ΔCD had positive and linear correlations with the global, semi-local, and local levels, which was consistent with the trend of the by-product ($SiBr_x$) intensity and with that of the taper angles of the etched profiles. We also clarified that ΔCD was affected by the amount of $SiBr_x$ generated within several times of the mean free path area for the semi-local dependence, and that it was the solid angle (S) viewing from a pattern, not the pattern space, that had a good correlation with variations in ΔCD as a control indicator. We used this experimental knowledge to model the $SiBr_x$ flux and created a Si gate etching simulation that demonstrated the ΔCD value and etched profile trends. We also found that Δd_R depended on $(R_G+R_S)S$ as well as on the dosage of incident particles, considering the relationship between d_R and the ion energy reduced by the $SiBr_x$ deposition depth [3]. Furthermore, when we used the analytical transistor model [3], we could predict ΔV_{th} and ΔI_{off} enhanced by the Si recess with $(R_G+R_S)S$.

These results show that it is crucial to control plasma processes such as ion energy, gas flux, and over-etch time considering the effect of pattern dependence of fluctuations in ΔCDand the Si recess.

[1] T. Ohchi et al., JJAP 47, 5324 (2008).

[2] T. Ito et al., JJAP 50, 08KD02 (2011).

[3] K. Eriguchi et al., JJAP 49, 08JC02 (2010).

9:20am **PS2-ThM5 Control of Surface Properties on Plasma-Etched Gallium Nitride (GaN)**, *R. Kometani, S. Chen, J. Park, J. Cao, Y. Lu, K. Ishikawa, K. Takeda, H. Kondo, H. Amano,* ***M. Sekine***, *M. Hori*, Nagoya University, Japan

Introduction - In plasma etching of gallium nitride (GaN), surface of GaN was etched by preferentially desorbed nitrogen [1] and roughened by bombarded by energetic ions at elevated temperature [2]. In this paper, we have studied about effects of temperature to form surface properties such as surface roughness.

Experimental - Samples were Si-doped GaN epitaxial layer with thickness of 1 μm grown by metal organic chemical vapor deposition (MOCVD) on sapphire substrates. After removed native oxides off chemically, the samples of GaN were partially etched off by using capacitively coupled plasma (CCP) reactor. Pure argon gas of 50 sccm was introduced and a pressure of 10 Pa was maintained. Plasmas were sustained by applying radio frequency (13.56 MHz or 100 MHz) power to a sample stage which temperature was maintained at 600°C. After the plasma processes for 10 min., morphology of the sample was measured by the atomic force microscopy (AFM), chemical composition was evaluated by the x-ray photoelectron spectroscopy (XPS).

AFM images of initial sample was shown smooth surface and also surface morphology was not significantly changed Just after annealed at 600°C for 10 min. However, after exposed Ar plasma at elevated temperature of 600°C for 10min, surface roughness was observed in particular. This is considered that the observed roughness caused by forming metallic-Ga precipitates on the surface, which was supported by results increase of metallic Ga bonding by XPS analysis. Namely, this indicates that favorable volatilization of nitrogen created Ga-droplets and promoted to roughen the surface at 600°C.

On contrary, surface morphology after N_2 plasma was relatively smooth although the high temperature. The results in smoothness were possibly resulted by difference in Ga droplet formation because of suppression of metallic Ga formation by reacting of reactive N species.

In this study, we report a method to control surface properties on plasma etched GaN through experiments carried out with samples at elevated temperatures. Further detailed discussion will be conducted.

Acknowledgement - This work was partly supported by the Knowledge Cluster Initiative (Second Stage)-Tokai Region Nanotechnology Manufacturing Cluster.

1) R. Kawakami *et al*., Thin Solid Film. **516**, 3478 (2008).

2) R. Kometani *et al*., Jpn. Soc. Appl. Phys. Spring Meeting (2012), 30a-M-11.

10:40am **PS2-ThM9 Theoretical Calculation of Neutralization Efficiency of Positive and Negative Chlorine Ions with Consideration of Excited States**, ***S. Ohtsuka***, *N. Watanabe,* Mizuho Information & Research Institute, Inc., Japan, *T. Kubota,* Tohoku University, Japan, *T. Iwasaki, Y. Iriye, K. Ono,* Mizuho Information & Research Institute, Inc., Japan, *S. Samukawa*, Tohoku University, Japan

We investigated the generation mechanism of neutral particles in high efficiency neutral beam source developed by Samukawa et al [1], by collision of positive and negative chlorine ions against graphite surface. It is already known experimentally that neutralization efficiency of negative ion (Cl-) is much higher than that of positive ion (Cl2+) [2] and that realized high efficiency and low energy neutral beam by usage of negative ions generated in pulse-time-modulated plasma. However, the mechanism has not been clarified. Recently we investigated the neutralization mechanism by using numerical simulations based on quantum mechanics [3-5] and succeeded in explaining higher neutralization efficiency of negative ions than positive ions. In this study, to obtain more reliable neutralization efficiency, we introduced consideration of excited states. A unit cell with a graphite surface and a chlorine particle (Cl, Cl+, Cl-, Cl2, or Cl2+) was used for the calculation. During a collision of the particle against the graphite, time evolution of wave functions of ion and graphite electrons was calculated by solving TD-Kohn-Sham equation [3, 4]. The probability of neutralization of an ion was estimated by calculating electron occupation numbers of each electron on each occupied and unoccupied molecular orbital. As a result, neutralization efficiencies of Cl- and Cl2+ ions were calculated as 87% and 77%, respectively. This result is consistent with our previous result that negative ions have higher neutralization efficiency due

to resonant neutralization mechanism than that of positive ions with Auger neutralization mechanism. It was also found that electrons of the neutralized Cl2+ occupied some unoccupied orbitals of the grounded Cl2, namely Cl2+ became excited Cl2* by the collision. On the other hand, electrons of the neutralized Cl- did not occupy unoccupied orbitals of the grounded Cl, namely Cl- became grounded Cl by the collision. Since excited Cl2* are likely to be re-ionized to Cl2+ by the following collisions, so we consider the re-ionization process should be also an important factor to estimate the neutralization probability of Cl2+ ion. A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).[1] S. Samukawa et al, Jpn. J. Appl. Phys. **40**, L779 (2001).[2] S. Samukawa, Jpn. J. Appl. Phys. **45**, 2395 (2006).[3] N. Watanabe et al., Phys. Rev. E **65**, 036705 (2002).[4] http://www.mizuho-ir.co.jp/solution/research/semiconductor/nano[5] T. Kubota et al., J. Phys. D: Appl. Phys. **45**, 095202 (2012).

11:00am **PS2-ThM10 High-aspect Ratio and Diameter Controlled GaAs/AlGaAs Nano-Pillar Fabrication using Defect-free Neutral Beam Etching and Bio-template Process**, ***Y. Tamura***, *M. Igarashi, M.E. Fauzi, W. Hu,* Tohoku University, Japan*, I. Yamashita,* Nara Institute of Science and Technology, Japan*, S. Samukawa*, Tohoku University, Japan

The III-V compound quantum dot (QD) has recently become extremely attractive when researching the quantum effect and developing novel opt/electronic devices such as high-efficiency intermediate-band solar cells. In the latter one, it is very important to precisely control the geometry size and alignment of QDs to form an intermediate-band. A high in-plane density is also necessary for photovoltaic devices in order to obtain a large optical gain. Molecular beam epitaxy have widely used and have been greatly researched for forming QDs. However, it is still a great challenge for realizing ideal nanostructures using self-organized bottom-up processes.

Our proposed top-down process of using bio-template [1] and neutral beam etching (NBE) [2] has great potential to fabricate defect-free, high-density (more than 7×10^{11} cm^{-2}), sub-20-nm-in-diameter GaAs QDs structures [3]. This process uses 7-nm-in-diameter iron cores of ferritin (protein included iron core) as the etching mask and damage-free NB with eliminating UV photons and high-energy ions to etch GaAs without defects.

In this study, we successfully fabricated high aspect ratio nano-pillars etched the GaAs/AlGaAs stack-layered structure with 95 nm height and 15 nm the diameter by using a NBE. The diameter of the GaAs nanodisk could be precisely controlled from 12 to 18 nm by a combination of Hydrogen-radical treatment and Cl_2-NBE. This is because a taper profile of GaAs-NBO film could be controlled by Hydrogen-radical treatment time due to the isotropic and slow etching rate. In addition, not only iron cores but also this tapered GaAs-NBO film can work as etching masks because of the high NBE selectivity of GaAs-NBO. Thus, the diameter of the GaAs nanodisk could be controlled using the surface GaAs-NBO film taper profile produced by the prior Hydrogen-radical treatment time before NBE. This result means that our fabricated nanodisk array structures have great potential for high performance III-V compound optical QDs devices.

[1] I. Yamashita. Thin Solid Films. **393**. 12. (2001).

[2] S. Samukawa. Jpn. J. Appl. Phys. **45**. 2395. (2006).

[3] X. Y. Wang, et al., Nanotechnology, **22**. 365301. (2011).

11:20am **PS2-ThM11 3-Dimensional and Defect-free Neutral Beam Etching for MEMS Applications**, ***Y. Yanagisawa,*** Tohoku University, Japan*, T. Kubota,* Tohoku University and BEANS Project, Japan*, B. Altansukh,* Tohoku University, Japan*, K. Miwa,* BEANS Project, Japan*, S. Samukawa*, Tohoku University and BEANS Project, Japan

To fabricate MEMS devices, it is necessary to etch large-scale three-dimensional (3D) structures. Plasma etching is widely used for this purpose, but plasma irradiates charged particles and high energy UV photons and they may cause problems.

Ion sheath exists between bulk plasma and the etched sample. It accelerates and collimates ions in plasma and enables vertical etching. However, when the sample has large-scale 3D structure whose height is similar to or larger than the sheath thickness, the sheath is distorted along the surface. This causes distorted acceleration of ions and results in distorted etching shape. Also, high energy UV photons from plasma generates defects and deteriorates the mechanical property. It is reported that quality factor (q factor) and resonance frequency (f) were decreased by plasma irradiation [1]. In this study, we investigated 3D, damage-free, and high aspect ratio silicon etching for MEMS application using neutral beam (NB) to solve these problems. NB source developed by Samukawa et al. [2] can achieve high neutralization efficiency and elimination of UV irradiation damage.

First, large-scale 3D structure etching was investigated by using a sample with a vertical step of up to 725 µm high. In cases of plasma etchings (Cl_2 ICP etching and Bosch process), distortion of etching shape was observed. The etching shape distortion is concluded to be due to ion sheath distortion, based on the dependence on the step height and plasma parameters. On the other hands, no distortion was observed in the case of NB etching. This is because accelerated and collimated neutral particles without electric charge are used in NB etching.

Next, etching damage on mechanical property of silicon was investigated using microcantilever structure. Ar plasma and neutral beam were irradiated at the surface of the samples. Plasma irradiation degraded q factor and f of the cantilever, but neutral beam did not. This is due to crystalline defects generated by the UV irradiation from plasma. It is regarded that phonons are scattered by these defects, which causes loss of vibration energy and decrease of q factor and f.

In conclusion, MEMS process suffers both of sheath distortion and UV irradiation problems and neutral beam can solve these problems.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO). This work is partly supported by Creation of Innovation Centers for Advanced Interdisciplinary Research Areas Program.

[1] M. Tomura et al., Jpn. J. Appl. Phys. 40, 04DL20 (2010).

[2] S. Samukawa et al., Jpn. J. Appl. Phys. 40, L779 (2001).

Plasma Science and Technology
Room: 25 - Session PS-ThA

Plasma Sources
Moderator: M. Funk, Tokyo Electron America

2:00pm **PS-ThA1 Study on Microwave ECR Plasma Source for 450-mm Wafer Etching**, ***K. Maeda***, Hitachi, Ltd., Japan, *H. Tamura, S. Obama, M. Izawa,* Hitachi High-Technologies Corp., Japan, *G. Miya*, Hitachi, Ltd., Japan **INVITED**

In semiconductor industries, a high level of productivity to reduce the cost of ULSI fabrication has always been required for plasma etching tools, as well as the other tools. According to the International Technology Roadmap for Semiconductors (ITRS) 2010, increasing the size of the wafer improves the productivity, and the diameter of the Si wafer will be 450 mm in 2014. One of the most significant problems for achieving an extremely uniform process for the 450-mm wafer area is precise control of the plasma distribution over a large area. We have developed a newly designed microwave electron cyclotron resonance (M-ECR) plasma reactor for next-generation 450-mm wafer processing. The reactor configuration is based on the previous M-ECR etching reactor for 300-mm wafers. A microwave power of 2.45-GHz in a circular TE11 mode (principal mode) is supplied to the chamber via the circular waveguide, microwave circuit (cavity), and quartz window. The chamber is surrounded by solenoid coils and a yoke, and the position of the ECR plane (87.5 mT magnetic field strength) is controlled by the currents supplied to the coils.

We present the measurement of two-dimensional (radial and vertical) distribution of ion saturation currents in the reactor, which was measured by a movable single probe system in halogen gas mixture at 0.4 Pa for poly-Si etching. The ring-shaped high density region was observed at the ECR plane in the optimized microwave circuit type, in which we could obtain uniform plasma distribution just above the wafer. This plasma distribution could be controlled by changing the position of the ECR plane. On the other hand, strongly convex-shaped plasma distribution was observed in an inappropriately designed microwave circuit. A plasma generating distribution is also estimated by comparing the result of plasma-diffusion analysis in magnetized plasma to that of a probe experiment. We confirmed that the plasma seemed to be generated in a very thin (1-2 cm) region at the ECR position. In addition to the result of plasma characteristics, the etching results, i.e., radial distribution of poly-Si etching rate, with a uniformity of 1.5%, and critical dimension control of the line and space pattern by controlling the temperature of the wafer are also presented.

2:40pm **PS-ThA3 A Grid Reactor with Low Ion Energy Bombardment for Large Area PECVD of Thin Film Silicon Solar Cells**, ***M. Chesaux***, *A.A. Howling,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *U. Kroll, D. Dominé,* Oerlikon Solar-Lab SA, Switzerland, *Ch. Hollenstein*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

This study presents a PECVD reactor using localized remote plasma in a grid electrode. The aim is to reduce the ion energy bombardment inherent in RF capacitively-coupled parallel plate reactors conventionally used to deposit large area thin film silicon solar cells. This bombardment could cause defects in silicon layers and deteriorate electrical interfaces. Here, low ion bombardment energy is obtained by inserting a grounded grid close to the RF electrode of a parallel plate reactor. The plasma is then localized in the grid holes and remote from the substrate. This grid also increases the negative self-bias by increasing the effective area of grounded electrode in contact with the plasma while retaining the lateral uniformity required for large area deposition. The self-bias reduces the ion energy bombardment, but retarding field energy analyzer measurements show that the ion energy is even lower than expected from the self-bias effect alone. This reduced ion energy could be caused by a non sinusoidal RF cycle of the plasma potential as was measured with a capacitive probe and supported by phase resolved optical emission spectroscopy. Measurements were done in hydrogen at 0.5 mbar and 13.56 MHz.

3:00pm **PS-ThA4 Plasma Generation and Delivery from a VHF Remote Source**, ***D. Carter***, *D. Hoffman, K. Peterson, R. Grilley*, Advanced Energy Industries Inc.

A new remote plasma source (RPS) driven by capacitively coupled VHF power has been defined for use in chamber cleaning or other processes where ex-situ plasma generation is desired. The combination of VHF drive, compact size and unique geometry results in a plasma source capable of very high plasma densities and a resulting field structure offering some interesting characteristics. The device is shown to allow operation in a conventional “remote” mode where the plasma is largely confined within the primary volume of the source or alternatively in a “projecting” mode where the plasma extends well beyond the output of the device reaching to and even filling a downstream chamber with active plasma. This study evaluates behaviors of the VHF RPS in both remote and projected modes as well as in a hybrid mix of both modes. We report on operating characteristics and plasma parameters including density, potential and electron temperatures at the source and downstream and additionally look at ion energy distributions at various points in the system. Results are compared with alternative remote source technologies to illustrate the differences and potential advantages offered by this new RPS topology.

3:40pm **PS-ThA6 Mechanical Optimization of a Plasma Source Device**, ***S. Polak***, *M. Thornton, D. Hoffman, D. Carter*, Advanced Energy Industries Inc.

A new, remote plasma source device (RPS) is being developed. From a mechanical standpoint, there are a number of unique challenges and areas for optimization. The RPS features high plasma density in a compact, mechanical envelope, resulting in high heat-flux and therefore requiring robust cooling solutions. Also, because the RPS has the ability to confine plasma within the chamber or project the plasma downstream, the locations and magnitudes of heat flux are dynamic, depending on the process. High and variable-density heat fluxes result in high temperatures and high thermal gradients, both of which lead to thermal-mechanical strain and stress within the components. Numerical models and finite-element simulations have been developed to predict the thermal and structural responses within the critical components in the RPS assembly and to mitigate structural failure of these components. Furthermore, because the RPS features high gas flow rates through a relatively small-volume chamber, optimization of the fluid flow becomes paramount to the ignition, stability, and efficiency of the plasma. Finite-volume, computational fluid dynamics (CFD) models were developed to characterize and optimize the gas flow into the chamber. We report on the development of these thermal-mechanical and fluid dynamics analysis tools, including correlation of the analytical models to empirical data. Also, we will discuss the parameters and techniques of optimization.

4:20pm **PS-ThA8 Impact of Reactor Design on Plasma Polymerization Processes - An International Round-Robin Study**, ***J.D. Whittle***, *A. Michelmore, D.A. Steele, R.D. Short*, University of South Australia

Plasma polymerization is capable of producing adherent pinhole-free thin films with a diverse range of chemical functional groups and physical properties. These materials are used widely in applications ranging from composites, electronics, solar cells and biomaterials. Although a number of plasma processes have been scaled up very successfully and have used sophisticated diagnostics, the majority of researchers utilize lab-built reactor systems with very little in the way of plasma diagnostics, relying on control of external parameters to achieve reproducibility and to guide materials design. Often the focus is on retaining chemical function from the precursor compounds, and these processes are typically described by a limited number of variables, for example, rf power, reactor pressure, monomer flow rate. While these parameters often give reasonable control within a given system, it is not clear to what extent these parameters correlate between systems.This becomes a problem when comparing plasma polymerisation experiments with those in the literature - generally the only practical way to repeat a treatment is to re-engineer the process on ones own system by a trial and error process.

In this paper we report the results of an international round-robin exercise which sought to explore the differences resulting from plasma polymerization using 14 different reactor designs spread across seven countries.

We have explored two separate processes; argon plasma treatment of spin-cast polystyrene films and deposition of plasma polymerized acrylic acid at different discharge powers. In all experiments the monomer or gas flow rate was kept the same, and treatments were carried out at the same nominal power. Surfaces were characterized using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), and the effect of reactor geometry, and other uncontrolled variables on the resulting surface properties was examined.

Whilst we did expect significant differences between these systems, the magnitude of these variations was surprising - for many of the surface properties, the coefficient of variation was in excess of 100%. We speculate on the key factors which influence the observed differences in the resulting surface treatment, and how these differences could be reduced in the future.

4:40pm **PS-ThA9 A Mini Plasma Source for *In Situ* Sample Cleaning**, ***N.B. Koster***, *F.T. Molkenboer, R.J. Bolt, T.J. Versloot, J.P.B. Janssen*, TNO Technical Sciences, The Netherlands

Energetic photons, ions and electrons can induce carbon growth on surfaces due to residual hydrocarbons present on the sample surface or in the vacuum system. This effect is well known and has been a major obstacle for the successful introduction of EUV Lithography. This has been overcome by introducing a very clean vacuum system in combination with surface cleaning technologies. For EUVL we have developed a plasma cleaning process for the mirrors that has a relatively high efficiency for carbon removal and causes no surface damage[1]. In high resolution imaging applications like SEM, TEM or Helium Ion Microscopy (HIM) this problem is also present and more difficult to counteract due to the delicate nature of samples or that the sample itself is the source of contaminants. We have applied our cleaning process and successfully and non-intrusively cleaned samples for electron microscopes. As a result, and on request of several microscopy users, we have developed a miniature microwave-induced plasma source to be used on various types of imaging systems for sample and chamber cleaning. The miniature source is to be mounted on the load lock of the imaging system or on the microscope chamber by means of a standardized vacuum flange.

We will report on the design, manufacturing and realization of such a miniature source and discuss the results that were obtained on our own HIM as well as other microscopes. This plasma process has already successfully been used to clean samples with graphene, EUV reticle materials or asbestos. Part of the experiments presented include characterization of the plasma with Langmuir probes and Optical Emission Spectroscopy (OES).

[1] N.B. Koster et al, Towards defect free EUVL reticles: carbon and particle removal by single dry cleaning process, and pattern repair by HIM , Proc. of SPIE Vol. 7969 79690X-1, 2011

5:00pm **PS-ThA10 Magnetic Neutral Loop Discharge Reactor for Low-k Dielectric Plasma Processing**, ***W.Y. Li***, *Z. Ling, H.-Z. Zhang, J.A. Bray, T.M. Griffin, M.T. Nichols,* University of Wisconsin-Madison, *B.N. Moon, Y.M. Sung,* Kyungsung University, Korea, *S. Banna,* Applied Materials, Inc., *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Since the magnetic Neutral-Loop Discharge (NLD) plasma was first proposed by Uchida *et al.* [1], its properties and usage have been investigated by a number of researchers. In this work, we design an NLD reactor to investigate the response of low-k dielectric materials to plasma exposure. Moreover, the NLD reactor will be used to compare the properties of its plasma to that of conventional inductively and capacitively coupled plasma reactors. The NLD reactor is located inside of a set of cylindrical magnet coils which at first glance appears to be a simple solenoid. However, the magnet current in the center of the solenoid is reversed from that near the ends of the solenoid which causes the field in the central solenoid to reverse from that in the outer solenoids. By carefully adjusting the coil currents, a circular region of zero magnetic field can be generated underneath the center solenoid—the neutral loop. The shape of the NLD magnetic fields was numerically evaluated and experimentally confirmed. Numerical calculations of particle orbits show the effect of the neutral-loop zero-field region. A region of electron cyclotron resonance appears around the neutral loop. By adjusting the currents, the radius of the neutral loop can be controlled to move closer or farther from the central axis of the reactor.

This work has been supported by Semiconductor Research Corporation under Contract No. 2008-KJ-1781 and by the National Science Foundation under Grant CBET-1066231.

[1] T. Uchida, "Application of radio-frequency discharged plasma produced in closed magnetic neutral line for plasma processing," 33, L43-L44 (1994).

5:20pm **PS-ThA11 High Efficiency ICP Source for Plasma Dry Clean Processing**, ***V. Nagorny***, *O. Todor, V. Surla, A. Kadavanich*, Mattson Technology, Inc.

Inductively coupled plasma (ICP) sources are widely used in the semiconductor industry for plasma processing. They can easily produce high density plasma and provide good plasma control. For photoresist strip (dry clean) processes, direct plasma interaction with a wafer is undesirable and plasma is used as an intermediate for modification of a gas composition and creating chemically active radicals for processing the wafers. As strip rate directly relates to the flux of radicals to the surface of the wafer this process usually uses high gas flows (5-20slm), high RF power (3-5kW) and high gas pressure (~1000mTorr). Obviously, when the gas and energy consumption is that high, the efficiency of the source becomes very important, since it affects both capital and operational costs, and with newer and more restrictive regulations, efficiency may become determining characteristic of the source.

There are a few factors that strongly affect source efficiency, as well as the process, the most important of which are the gas flow and electron heating efficiency. If only small fraction of gas molecules participate in collisions with hot electrons then most of the gas simply flows through the system without dissociation. In this case most of the gas is simply wasted. So it is important to make the gas flow in such a way that most (if not all) gas molecules have a high probability of collision with hot electrons. To increase efficiency of generating hot electrons one has to improve electron confinement in the region where the induced electric field is high.

We accomplished both goals by modifying Mattson Technology Inc.'s production-proven ICP strip source. By modifying the gas injection system into the plasma generating volume and optimizing the vessel, we simultaneously achieved significantly increased photoresist removal rate at reduced input of process gas and a much larger operational window for the source, with concomitant process benefits.

Our implementation is scalable for processing 450mm wafer sizes and the underlying concepts are generalizable for optimizing other types of ICP sources, as will be discussed in the presentation.

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

Plasma Science and Technology Poster Session

PS-ThP1 Plasma Etch Challenges to Produce Metallization-Friendly Profiles at 20nm and Beyond Technology Nodes in the BEOL, ***Y. Mignot***, STMicroelectronics, *R. Koshy,* GLOBALFOUNDRIES, *Y. Park,* Samsung Electronics Co. Ltd., *R. Srivastava,* GLOBALFOUNDRIES, *E. Soda,* Renesas Electronics, *Y. Yin, M. Beard, B.G. Morris,* IBM Microelectronics, *K. Trevino,* GLOBALFOUNDRIES, *J. Arnold, S. Allen,* IBM Microelectronics, *C. Labelle,* GLOBALFOUNDRIES, *M. Sankarapandian,* IBM Microelectronics, *Y. Loquet,* STMicroelectronics, *Y. Feurprier, L. Wang, J. Stillahn, Y. Chiba, V. Gizzo, K. Kumar,* Tokyo Electron Technology Center, America, LLC, *C.A. Wang, Q. Zhang,* GLOBALFOUNDRIES, *A. Inada,* Renesas Electronics, *S. Mignot*, STMicroelectronics

As feature critical dimension (CD) shrinks towards and beyond the 14nm node, new patterning techniques within the context of a trench-first-metal-hard-mask (TFMHM) patterning scheme have been developed to generate trenches and vias below 100nm pitch. One of the main challenges at advanced nodes is to create structures (i.e., trenches & vias) that can be robustly metalized This requires several elements of focus for the etches: first, there must be zero dielectric etch damage that results in undercut of any hard masks in the film stack; second, the aspect ratio of the final etch structure must be minimized; and third, the shape of the trench or via profile must be tailored to be metallization-friendly (i.e., slight angle better than vertical). These requirements often conflict with each other, especially within a patterning scheme that requires self-aligned vias, where the desired high selectivity to the hard mask conflicts with the need to minimize the amount of hard mask left in order to decrease aspect ratio. In this paper, we will discuss some of the approaches that we have investigated to achieve the best profile for metallization. This includes plasma etch all-in-one (AIO) dielectric etch optimization as well as multi-step solutions that potentially can use techniques including wet chemistries, ion beam metal etching, and dry metal etching. In addition, data will be presented on efforts to minimize overall metal-related residues observed as a function of the pattern density and thus, metal exposure. Metal-containing etch byproducts have also been observed and the material characteristics and/or morphology of these etch byproducts can vary across the wafer, producing non-uniform residue patterns and affecting the plasma etch erosion of the metal hard mask itself. Understanding the underlying mechanisms of observed metal-induced defects (i.e., residues, etch byproducts, etc.) is key to applying the correct plasma etch optimization to eliminate or minimize the effects. Some data will be presented showing the progress that has been made on these issues.

PS-ThP2 A Comparative Study of Plasma-Treated Fluoropolymers at Atmospheric Pressure, ***T. Dufour***, *J. Hubert, N. Vandencasteele, F. Reniers*, Université Libre de Bruxelles, Belgium

Due to their extraordinary range of properties, polymeric materials play an essential and ubiquitous role in everyday life. Plasma-modifications of polymeric surfaces further extend the range of their applications, especially with fluoropolymers due to their widespread in biocompatibility and self-cleaning coatings applications.

The aim of our work is to compare the treatments carried out with two distinct plasma sources on a selection of fluoropolymers: PVF, PVDF, TrFE, PTFE, Nafion©, FEP and PFA. The first treatment is performed with a post-discharge generated by an RF plasma torch, supplied with a helium-oxygen mixture and operating at atmospheric pressure. The second treatment is achieved in the plasma phase of a DBD and operates at atmospheric pressure, also in the same gases. In both cases, we discuss the influence of the treatment time and of the O_2 flow rate on the surface properties. A comprehensive study of the plasma/polymer interface has also been performed by mass spectrometry and optical emission spectroscopy to identify the species responsible of the surface texturization, i.e. the species breaking the atomic bindings on the surface top atomic layers.

The surface properties are characterized by determining the advancing and receding WCA so as to show if the treated polymers can be classified into the Wenzel or Cassie-Baxter models. The super-hydrophobicity of PTFE has already been achieved. Moreover, two liquid probes have been used: milliQ water (H_2O) and diiodomethane (CH_2I_2) to discuss the validity of the Fowkes theory.

Finally, the XPS analyses give information on the surface composition which remains unchanged for the majority of the studied fluoropolymers. We will also explain how it is possible to identify the fragments ejected from the polymeric surfaces during the etching process by using the XPS instrument. CF_2 fragments have already been evidenced in the case of the PTFE and different ones in the case of Nafion©.

PS-ThP3 Advances in 2D/3D Feature Profile Simulations, ***P. Moroz***, Tokyo Electron US Holdings Ltd

Plasma etching, deposition, and implantation are widely used in semiconductor industry, with application of complex chemistries and plasmas to obtain desirable profiles and material properties. However, in practice, etched profiles might show undesirable effects such as bowing, or necking, or micro-trenching, among others, as well as might demonstrate the so-called loading effect. Those effects become more concerning or even dangerous for features of smaller sizes, especially for high aspect ratio etching of trenches and contact holes where they could lead to defects of the device. Selecting proper gas mixtures as well as the regimes of plasma operation to obtain proper profiles is a very tedious process, and numerical simulation could become a highly needed and useful tool. Here we discuss new capabilities and unique characteristics of the 2D/3D feature profile simulator FPS-3D [1-2]. The FPS-3D simulator was developed as a general type simulator, in principle, applicable to any materials, reactive gases, plasmas, or beams, for which the user could provide proper reaction mechanisms. FPS-3D can simulate etching, deposition, or implantation processes going on at the same time. Among new developments to be presented is the capability of considering multi-step (or multi-recipe) processes, when each step could have different fluxes to the surface and different chemistry. Another new development in FPS-3D is the possibility of simulating the pulse-plasma effects. Examples presented are mainly based around a particular case of HARC etching of SiO2 by the fluorocarbon-argon-oxygen plasma in a capacitive-type plasma system. [1] P. Moroz, ECS Transactions, 35 (20) 25 (2011).[2] P. Moroz, IEEE Transactions of Plasma Science, 39 (11) 2804 (2011).

PS-ThP4 Laser Thomson Scattering Measurements of Plasma Parameters in the Low Temperature Plasmas, ***J.-H. Kim***, Korea Reseach Institute of Standards and Science, Republic of Korea, *B.H. Seo,* Korea Advanced Institute of Science and Technology, Republic of Korea, *S.-J. You, D.J. Seong*, Korea Reseach Institute of Standards and Science, Republic of Korea

Diagnostics of electron density and temperature play an important role for characterization of processing plasmas and basic plasma researches. Laser Thomson scattering is a one of the most accurate diagnostic technique for measuring electron density and temperature because of none-perturbation to plasma among various diagnostic techniques invented to measure plasma density and temperature. I will briefly review the method of Laser Thomson Scattering to measure the electron temperature and density. Electron energy probability functions (EEPFs) having a fine resolution of electron energy were measured in low-pressure inductively coupled plasma with laser Thomson scattering method (LTS) at various plasma conditions (rf powers and gas pressures) and compared with the EEPFs measured by a single Langmuir probe (SLP) at the same experimental conditions. The result of LTS showed that the measured electron density normally increases with the rf power and the gas pressure, and the electron temperature decreased with the rf power and the gas pressure. The results have a good agreement not only with the previous reports qualitatively but also with our SLP measurement result quantitatively. We have a plan to establish a standard of plasma measurement with this LTS, which will be discussed.

PS-ThP5 Development of a New Plasma Treatment Followed by a Bake for Photoresist Linewidth Roughness Smoothening, ***M. Fouchier***, *E. Pargon,* CNRS/UJF-Grenoble1/CEA LTM, France, *L. Azarnouche,* ST Microelectronics, France, *K. Menguelti, M. Brihoum*, CNRS/UJF-Grenoble1/CEA LTM, France

As the dimensions of microelectronic circuits scale down, the gate linewidth roughness (LWR) increasingly impacts the electrical performances of transistors. It has previously been shown that the significant photoresist (PR) sidewall roughness after lithography is transferred into the gate during the subsequent plasma etching process, resulting in a final gate LWR far above the ITRS requirements. The key to reduce the gate LWR is to minimize the photoresist LWR before plasma transfer. Plasma treatments are commonly used for that purpose. In previous studies, we have shown that photoetching mechanisms occurring during plasma exposure plays a key role in PR smoothening. We have also demonstrated that the carbon species outgassed during the treatment can redeposit on the PR pattern sidewalls and degrade the LWR. Moreover, we have shown the benefit of applying a bake after plasma treatment in order to further decrease the LWR. From this knowledge, we develop a new treatment based on HBr/O₂ plasma exposure followed by a bake. The plasma

conditions are optimized in order to emit strongly in the vacuum ultra violet (VUV) range (below 200 nm) and to prevent carbon redeposition on the resist sidewalls. We show that by controlling the VUV dose (mainly by tuning source power or plasma exposure time), the PR bulk can be either softened (photolysis) or strengthened (crosslinking). Moreover, the formation of the carbon deposit on the resist surface can be controlled by the O₂ content of the plasma. The surface and bulk properties of the PR line after plasma treatment will determine the LWR behavior during the subsequent thermal cure treatment. A soft resist bulk combined with a thin surface carbon layer is the ideal case to get the best LWR smoothening during the bake without reflowing. By optimizing both the plasma oxygen content and VUV dose, we obtain a 60% LWR decrease after bake reducing the LWR from 7.3 nm to 2.9 nm.

PS-ThP6 Analysis of Target Oxidation in Reactive Sputter Deposition Processes of Silicon Dioxide*, **K. Hoshino**, K. Demura, S. Tamaya, M. Okamoto, Y. Murakami,* Canon Inc, Japan*, M. Isobe, T. Ito, K. Karahashi, S. Hamaguchi*, Osaka University, Japan

Reactive sputtering is widely used for thin film deposition of various compounds such as oxides and nitrides of metal and non-metal elements. In reactive sputtering processes, reactive gases such as oxygen are added to discharge of a sputtering system and chemical reactions between gaseous species and sputtered materials from the target form chemical compounds that are deposited on the substrate. In reactive sputtering processes, chemical compounds are also formed on the target surface and the thickness of the compound layer affects the sputtering rate of the target, which in turn can affect the film deposition rates and even film qualities. Therefore, for deposition of high quality thin films, control of compound formation on the sputter target is considered to be of significant importance.

Compound-layer formation on a target must be caused by influx of reactive ions and free radicals from the plasma despite the constant sputtering of the target surface. Details of such surface reaction processes have not been well understood to the extent that such knowledge could be readily used for the control of reactive sputter deposition processes.

In this work, we have focused on reactive sputtering deposition processes of SiO₂ thin films and examined the oxide layer formation on a Si target, using multi-beam injection experiments with beams of radicals and mass-analyzed energetic ions as well as molecular dynamics (MD) simulations of surface reactions. It has been found that oxygen ions, which penetrate the substrate more deeply than argon ions at the same incident energy, cause constant oxidation of the surface whereas the flux ratio of low-energy charge-neutral oxygen radicals to argon ions can also significantly affect the thickness of surface oxide. These results can be used to facilitate the control of plasma conditions for reactive sputter deposition processes.

PS-ThP7 On the Origin of the Line Width Roughness of Photoresist Patterns after Plasma Exposure*, **R. Ramos**, M. Brihoum, K. Menguelli, L. Azarnouche, M. Fouchier, E. Pargon, G. Cunge, O. Joubert*, LTM (CNRS / UJF-Grenoble1 / CEA), France

The control and minimization of the roughness on the sidewalls of transistor gates is a major aspect of the plasma patterning technology in microelectronics. The line width roughness (LWR) in the active layers is known to originate mostly from the transfer of the initial LWR of the photoresist patterns defined by 193 nm lithography. As a consequence, numerous plasma pre-treatments of the photoresist have been developed and applied to decrease the mask LWR prior to the plasma etching of the gate stack. However, the final LWR is still higher than the requirements for the next technological nodes. It is therefore necessary to develop a clear understanding of the physical mechanisms responsible for the modifications of the photoresist LWR during plasma exposure to further reduce the gate width roughness. In this work, we will show that plasma treatments of photoresist patterns result in the formation of a shell surrounding the pattern, i.e. including on surfaces not exposed to ion bombardment. The redeposition of by-products from the (photo)etching of the resist polymer plays a major role in the formation of this shell. We will highlight the influence of the mechanical properties of both the shell and the underlying modified photoresist on the LWR of plasma-exposed resist patterns. Based on the proposed mechanism, we will discuss the potential of pulsed plasmas for LWR reduction processes.

PS-ThP8 Effect of Film Properties on Nitride Etching*, **T. Wanifuchi**, G. Takaba, H. Ohtake, M. Sasaki*, Tokyo Electron Technology Development Institute, INC., Japan

Silicon nitride has been widely used for dielectrics of CMOS logic devices, especially, for spacers or stopper layers. However, the mechanism of etching was not known well. In addition, several kinds of nitride film have been used in the devices and we have to know the effect of film properties on the etching characteristics.In this paper, the effect of film properties on nitride etching characteristics was investigated. 5 kinds of nitride wafers were prepared by changing the deposition temperature. The film density was lower at the lower deposition temperature, which contains more hydrogen in the film. As etching tools, RLSA™ Etch, ICP and CCP were used. RLSA™ Etch has high Ne of more than 1×10^{11}cm^{-3} and low Te of less than 1 eV around the stage because RLSA™ Etch tool uses the surface wave plasma and diffusion chamber. CH_3F/ CF_4/ O_2 gas chemistry was used in all etchers. CCP showed ion-dominated etching because the etching rate was almost constant at various nitride films. On the other hand, RLSA™ Etch and ICP showed the dependence of etching rate on film property. The etching rate decreases by increasing the film density. However the RLSA™ Etch showed stronger dependency as compared with ICP. It is considered that radical- surface reaction dominated etching was realized at RLSA™ Etch because ICP generates fluorocarbon polymers more than RLSA™ Etch. Moreover, the dependency on film property was strongly related to the etching recipes. Film dependency was enhanced at the radical (chemical) etching condition as compared with ion dominated etching condition. In addition, we also observed the surface of nitride after oxygen plasma exposure because we used this plasma for surface cleaning. The results showed the dense and shallow oxidation layer was generated at the dense nitride film.Based on these result, we found that the etch characteristics was drastically changed by the film property and we have to use the appropriate plasma for precise nitride etching, corresponding to the film property.

PS-ThP9 A DC-RF Magnetized Plasma Source*, **Y. Raitses**, I.D. Kaganovich*, Princeton Plasma Physics Laboratory

We report results for a new plasma source which uses a low pressure (~10^{-4} Torr) discharge with applied electric and magnetic fields. A dc voltage of 20-100 V is applied between the RF plasma cathode and the anode-chamber. The magnetic field is varied between 50-500 G. Under such conditions this cross-field discharge is shown to sustain an efficient ionization of xenon and argon gases (n_e^{max} ~ 10^{11}-10^{12} cm^{-3}, T_e~ 1-10 eV). Probe measurements revealed that the magnetized plasma of the DC-RF discharge has a non-Maxwellian EEDF with a depleted high-energy tail. It is also shown that spatial variations of the EEDF are governed by a non-local electron heating and anomalous electron transport across the magnetic field. An important implication of the above results is that the anomalous electron transport may degrade the magnetic filter effect, which supposes to separate “hot” and “cold” groups of plasma electrons.

This work was supported by the US DOE.

PS-ThP10 Quick Estimation of Deposition Rate for a Sputter System*, **G. Ding**, Y. Wang, J. Cheng, D. Schweigert, Z. Sun, M. Le*, Intermolecular Inc.

Here we present a practical estimation on deposition rate for a sputter system. The sputter system consists of four sputter sources in a high vacuum chamber, with an independent power supply for each sputter source. Quick estimation of deposition rate could be helpful for efficient experimental planning and reducing the number of experiments and time.

First, theory: Our early JAP paper* disclosed an energy balance model and derived a sputter rate = $k\ (P - P_o)$. The physical meaning is that the sputter rate has a linear relationship with plasma source power P, with a nearly constant offset P_o, and constant slope k. Here we present several different materials results which illustrate the good fit between deposition rate and power within the working range of 100W to 550W.

Second, P_o estimation: The physical meaning of P_o is the power consumed to sustain plasma, which is dependent on the plasma boundary condition (chamber/plasma source geometry), ion diffusion co-efficient, electron temperature etc. In this situation, since the plasma ion is primarily Agon ion with fixed chamber geometry, $P_o$is nearly constant within the range of 25 to 52 W. With a simple estimation of 39W, an error of only 13W could be introduced. For a typical 200~400W experimental condition, the error from this estimation is small (2~5% error).

Third, slope k estimation: The different materials trends with slope k are calculated $M/D *Y* V$ and plotted. (M: is the atomic weight, D: is the density, Y: is the sputter yield at 300V for Argon ion, and V is the DC voltage of the sputter source). The model assumes that the slope k is proportional to the sputter yield at the DC voltage, and converts the mass to volume for thin film thickness based on the deposition rate calculation. In our case, DC voltage V is close to 300V, so that sputter yields at 300V were used. However, further investigation showed that the simple sputter yield might not be accurate enough, and the correction for the sputter DC voltage could provide a better fit. The slope k trend agreed well with model estimation $M/D*Y *V$. Thus, results here implied that the slope k could be estimated for different materials.

Thus, a quick deposition rate estimation method was derived in comparison with experiments, which is expressed as:***dep rate= M/D*Y*V * k' *(P-P$_o$)***, and *K'* and P_o are chamber specific that need to be experimentally

determined. Once calibrated from one experiment, the deposition rates of other materials can be estimated from this formula.

In addition, this study could be helpful in applying to other chambers and sputter sources for a quick deposition rate estimation, even for alloy target or reactive sputtering.

PS-ThP12 Application of E-beam Curing Technique to EUV Resist Utilizing DC Superimposed Capacitively-Coupled Plasma, ***M. Honda****, T. Katsunuma, K. Narishige,* Tokyo Electron Miyagi Ltd., Japan*, K. Yatsuda*, Tokyo Electron Limited, Japan

EUV lithography provides much bigger dry etch challenges than 193-nm lithography did. Its depth of focus (DOF) is

so small that the thickness of EUV resist is much thinner than that of 193-nm resist. Although EUV resist requires

higher etch selectivity than 193-nm resist does, UV/VUV cure, which has been used in 193-nm resist, is not an

effective technique to enhance etch selectivity and physical strength. This is because UV/VUV light is essentially

transparent in EUV resist. Etch selectivity normally attributes to polymer which prevents material from being etched.

In the case of EUV resist, line width roughness (LWR) is easily enhanced by polymer because its physical strength

is so low, and the resist width is so small that the resist cannot tolerate the stress of polymer. This is quite contrary

to the ideal reactive ion etch (RIE) which diminishes LWR. Therefore, an alternative curing technique for EUV resist

is required to improve the etch selectivity without increasing LWR.

We introduced the e-beam curing technique for 193-nm resist utilizing a direct current superimposed (DCS) capacitively-coupled plasma (CCP) at the 55th AVS in 2008. Negative high DC voltage is applied in DCS CCP,

and positive ions collide with the upper electrode. Thus, secondary electrons are emitted from the upper electrode.

The applied negative high DC voltage also accelerates the emitted secondary electrons, which turn into ballistic

electrons. The curing mechanism of 193-nm resist is scission and cross-linking of polymer by e-beam which is a

consequence of ballistic electrons. Considering its mechanism, the e-beam curing should be available to any

polymer. Thus, we applied this technique to EUV resist, and investigated the effect of e-beam in EUV resist. In order

to identify the cured thickness and chemical structure change, the surface was analyzed with cross-sectional SEM

and ToF-SIMS, respectively. As a result, the curing effect was confirmed. In addition to the curing technique, we

also invented a coating technique with a silicon compound material by sputtering the upper electrode utilizing the

DCS technology. This coating technique increases the etch selectivity to EUV resist. In this technique, silane type

gases are not required, making it easily applicable to manufacturing.

PS-ThP13 SiH_4/H_2 and CH_4 Multi-Hollow Discharge Plasma CVD of SiC Nano-Composite Anode for High Charge-Discharge Capacity Lithium Ion Batteries*, **Y. Morita***, Kyushu University, Japan

Although most lithium ion batteries employ carbon in various forms such as graphite, hard carbon and microspheres, as an anode material; carbon has the low charge-discharge capacity up to 372 mAh/g. Silicon is one of the most attractive material to replace the carbon anode because it is abundant and has the high charge-discharge capacity up to 4200 mAh/g. Fully lithiated silicon is 4 times larger in volume than Si and such significant increase in volume causes fracture and pulverization of the electrode, thereby leading to capacity degradation and failure of battery cells. Recent studies showed that carbon-silicon composite material is effective to solve the silicon related problems. Here we employ SiC nanoparticles as an anode material [1]. Surface carbonization of silicon nanopartciles was performed using double multi-hollow discharges, where nanoparticle generation and the surface carbonization were independently controlled with the double multi-hollow discharges. Silicon nanoparticles were produced by the multi-hollow discharges of H2 + SiH4multi-hollow discharge plasma. CHx radicals for carbonization, which was produced by the CH4 multi-hollow discharge plasma, were irradiated to nanoparticles during their transportation to the downstream region. The electrolyte was 1M LiPF6 in ethylene carbonate (EC)/ dimethylene carbonate (DMC) (1:2). For measurements of anode properties, a Li metal sheet of 1 mm in thickness was used as a cathode [2]. Li intercalation capacity was measured with a constant current of 0.1 mA/mg. Charge-discharge capacity of the SiC nano-composite anode of the first cycle was 3000 mAh/g, which is 9 times higher than the capacity of graphite anode. SiC nano-particle-composite anode produced by plasma CVD is promising for lithium ion batteries. Lithium-ion batteries will play the most important role in the future of electric energy storage applications, including hybrid and electric vehicles over the next five years.

Work partly supported by Regional Innovation Strategy Support Program，MEXT.

[1] G. Uchida, et al., Jpn. J. Appl. Phys. 51 (2011) 01AD01-1.

[2] T. Ishihara, et al., Electrochem. Solid-State Lett., 10 (2007) A74.

PS-ThP14 Interface Trap Generation by VUV/UV Radiation from Fluorocarbon Plasma*, **M. Fukasawa***, Sony Corporation, Japan*, Y. Miyawaki, Y. Kondo, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine,* Nagoya University, Japan*, H. Matsugai, T. Honda, M. Minami, F. Uesawa,* Sony Corporation, Japan*, M. Hori,* Nagoya University, Japan*, T. Tatsumi*, Sony Corporation, Japan

Incident species from plasma needs to be strictly controlled to fabricate advanced devices. We found that simultaneous injection of VUV/UV radiation and radicals caused the marked etch rate enhancement of SiN_x:H films [1]. This indicates that not only ions, but also VUV/UV radiation affects the surface reaction of radicals with SiN_x:H. In this study, we investigated the effect of transmitted VUV/UV radiation on underlying interface traps of SiN_x:H/Si substrate by using the pallet for plasma evaluation (PAPE) [2].

A dual frequency (60/2 MHz) CCP reactor was used. SiN_x:H films were deposited on Si substrates by PECVD and those were exposed to CF_4/O_2 plasma. The thicknesses of SiN_x:H films were 200 nm. To investigate the effect of radiation, MgF_2 (> 115 nm), quartz (> 170 nm), and borosilicate crown glass BK7 (> 300 nm) windows were put directly on the SiN_x:H film. The capacitance-voltage (*C–V*) characteristics of SiN_x:H on Si substrate were analyzed to study the interface-trap density (D_{it}).

The penetration depths of photons strongly depend on the wavelength of the VUV/UV radiation and the absorption coefficient of materials. The wavelengths of photons were classified into three major ranges by their interaction with the material:

1) Photons are absorbed in the material and damage the film and/or enhance the surface reaction [1].

2) Photons are transmitted through the material and absorbed in the underlying interfaces, resulting in the increase in D_{it}.

3) Photons are transmitted through both the material and interface, and there is no impact on the damage generation.

The D_{it} increase is the most serious issue for advanced device fabrication since the D_{it} directly degrades electrical performance. Thus, the damage of SiN_x:H/Si substrate interface was investigated by *C–V* measurement. The D_{it} of SiN_x:H/Si substrate was unaffected by the VUV radiation (< 170 nm) since all the high-energy photons were absorbed in the SiN_x:H film (case 1). When the photons in the UV region (> 170 nm) were irradiated, the D_{it} increased and a negative charge was generated in the interface (case 2). This indicates that the VUV/UV radiation transmitting through the upper dielectrics causes the electrical characteristics of underlying devices to fluctuate. The UV radiation (> 300 nm) had almost no effect on the increase in D_{it} (case 3) due to the lack of absorption in both the material and interface.

Thus, the wavelength dependence of increases in D_{it} needs to be investigated for possible interfaces in advanced devices.

[1] M. Fukasawa *et al*., Jpn. J. Appl. Phys., 51 (2012) 026201.

[2] S. Uchida *et al*., J. Appl. Phys., 103 (2008) 073303.

PS-ThP15 Design of a Standalone Plasma Diagnostics Box*, **F.T. Molkenboer***, H.H.P.Th. Bekman, F.H. Elferink, T.J. Versloot, E. Te Sligte, N.B. Koster*, TNO Technical Sciences, The Netherlands

In setups for plasma research there are in most cases several sensors available to monitor the plasma conditions. However there are also numerous plasma systems for non-research applications that have limited or no plasma diagnostics available at all.

To solve this problem we have designed, a so called plasma diagnostics box. The plasma diagnostics box is made out of two units, a sensor head and the data logger box containing the data logger, batteries and electronics, connected by a flexible tube.

The sensor head contains multiple stand-alone sensors. The prototype device contains five basic plasma monitoring sensors, a PT100 temperature sensor, a heat flux sensor, silicon photodiode, a double Langmuir probe and a Faraday cup for measuring several key plasma parameters

The two unique features of the plasma diagnostics box is that it is a complete standalone unit and that it can be placed within the vacuum/ plasma system. This means that there is no need for a feedthrough flange on the plasma/ vacuum system. However, if a feedthrough is available, the data logger box can be placed outside the vacuum, and the sensor head alone can be inserted in the system.

Because of the flexible connection the sensor head can be placed anywhere within the plasma. This makes it possible to characterise the plasma at different positions.

In this contribution we will discuss the design and manufacturing of the plasma diagnostics box. Besides the design we also will present the data we have measured with the plasma diagnostics box in one of our research plasma setups that we have available at TNO. The results obtained with these measurements will be benchmarked against the commercially available diagnostics on our research plasma setup.

PS-ThP18 A New Compact ICP Source for Neutral and Ion Beam Extraction, ***E. Karakas***, *V.M. Donnelly, D.J. Economou*, University of Houston

A new compact inductively-coupled plasma (ICP) source will be presented. The source is designed to extract either a monochromatic ion beam or a neutral beam out of the plasma, to achieve highly selective etching of silicon, silicon nitride, or silicon dioxide. Two identical plasma sources were fabricated and installed on a processing chamber, with their axes perpendicular to one another. This setup offers flexibility in bombarding a substrate with neutrals and energetic ions either simultaneously, at a 450 angle of incidence, or sequentially at 900. Ion and neutral beams can be extracted in continuous or pulsed plasma modes. The sources can be characterized with line-of-sight mass spectroscopy, while etched surfaces can be examined by vacuum-transferred x-ray photon spectroscopy (XPS). A Langmuir probe was employed to measure spatially- and temporally-resolved plasma parameters as a function of pressure and power. At the center of the plasma, an electron density of 9.5× 1011 cm-3 was reached for 500 W input power at a pressure of 50 mTorr Ar. A retarding field ion energy analyzer was employed to measure the ion energy distributions (IEDs) on a grounded substrate. In a pulsed mode, when the electron temperature decreased to a low value late in the afterglow, a synchronous pulsed DC bias was applied to a boundary electrode, creating a monoenergetic ion beam at a peak energy that was nearly equal to the bias voltage. The IEDs showed a single peak with or without bias. Initial characterization of the neutral beam composition and etching of silicon will also be presented.

*Work supported by Lam Research Corp.

PS-ThP19 The Role of Ions in the Gas-Surface Interactions of Nitrogen Oxide Plasma Systems, ***J.M. Blechle***, *M.F. Cuddy, E.R. Fisher*, Colorado State University

Improving upon the effectiveness of substrates that are used in vehicular emissions abatement hinges on the ability to elucidate the contributions of various gas-phase species in surface reactions. Utilizing inductively coupled plasmas, the role of ions on surface reactivity is investigated to improve and tailor surfaces for the reduction of nitrogen oxide (N_xO_y) species. Here, nascent ions are monitored via mass spectrometry and energy analysis for NO, N_2O, NO_2, and a 50/50 mixture of N_2 and O_2 precursor gases. The mean ion energy ($\langle E_i \rangle_{total}$) determined for all ions within each respective plasma system shows a strong positive correlation with applied rf power and a negative correlation with system pressure for all precursors studied. Ions also play varying roles in the surface scatter of NO radicals as demonstrated by the imaging of radicals interacting with surfaces (IRIS) technique. The net effect of ions on surface processing is dependent upon plasma parameters including the choice of precursor gas. Scatter coefficients (S), determined for ion-limited plasma systems are compared to ion-rich systems to correlate $\langle E_i \rangle_{total}$ and scatter, which suggests a need for precise control of the chemistry occurring between the gas-phase and surface. Such information lends itself not only to the evaluation of plasma processing as a method of N_xO_y emission control, but also to improve current substrates and techniques.

PS-ThP21 Diagnosing Toroidally Confined Pure Electron Plasma using Electrostatic Waves, ***S.A. Exarhos***, *M.R. Stoneking, J.W. Darrell*, Lawrence University

Non-neutral plasma, or plasma made up of particles of a single sign of charge can be isolated and confined for long periods of time, permitting detailed examination. Non-neutral plasma possesses characteristics that are unique (such as a dynamic equilibrium state), while exhibiting some phenomena that are similar to neutral plasma (such as supporting the propagation of electrostatic waves). Previous work on non-neutral plasma has been conducted largely in cylindrical traps, but our toroidal trap offers the opportunity to test theoretical predictions that are not observable in cylindrical geometry. One such effect is the transport and mode damping due to a phenomenon called magnetic pumping. We report on experiments in which we excite toroidal analogs of two different so-called ‘diocotron’ (or flute-like) modes in the plasma in order to diagnose its characteristics and behavior. The frequency of the m=1 diocotron mode is proportional to the total trapped charge in the plasma. The damping of this mode has a strong dependence on magnetic field that is not presently understood, though theory suggests there is a dependence on, as yet unmeasured, plasma temperature. The frequency of the m=2 diocotron mode provides information about the average density of the plasma and its time variation, as well as its dependence on magnetic field, and other experimental control parameters. The combination of total charge and average plasma density provides a measure of plasma transport. This work is supported by National Science Foundation Grant No. PHY-0812893.

PS-ThP22 Diagnostic Studies of Ar/c-C_4F_8 Plasmas: The Effect of N_2-addition on Gas Phase and Surface Kinetics, ***P.K. Kao***, *Y.J. Yang*, National Taiwan University, Taiwan, Republic of China, *P.W. Chiou, C.C. Chou*, Tokyo Electron Taiwan Limited, Taiwan, Republic of China, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

The effects of N_2 addition on gas phase and surface kinetics in c-C_4F_8 and Ar-containing capacitively coupled plasmas are studied. The plasma is sustained using a 13.56-MHz rf power supply with an L-type matching network. Two systems with different geometries are utilized in this study. The first system consists of a cylindrical glass chamber with an annular ring-shaped powered electrode and a planar sample stage that serves as the grounding electrode. The second system is a parallel-plate discharge chamber with the electrode diameter 25.4 cm and the gap distance 60 mm. Optical emission spectroscopy is used to identify key species and to quantify gas temperature. The surface deposition is analyzed using XPS, FTIR, and SEM. Various solvents are used to test the chemical resistance of the deposited fluorocarbon film. Preliminary optical emission spectroscopic studies identified CN emission, which strongly suggests nitrogen incorporation into the gas phase reaction. The gas temperature is found to be between 1200 and 1350 K under 97 mT with 50 W power, and is found to be insensitive to N_2 addition. XPS analysis clearly shows the existence of the N peak, which clearly shows that nitrogen is involved in the surface kinetics. FTIR clearly shows the existence of stretching vibrations of CF_2 bond. Under 57 mT and 50 W power with Ar:C_4F_8=12:4 sccm, the surface fluorocarbon film deposition rate is approximately 25 nm/min. No major effect in this deposition rate is seen with up to 4 sccm of N_2 addition. The chemical resistance test shows that this deposited film is not resistant to acetone. This clearly demonstrates that the film is rather different from polytetrafluoroethylene film, which is resistant to various solvents including acetone. Finally, the implication of N_2 addition on the etching processes will be discussed.

PS-ThP23 Advanced Etch Profile Control and the Impact of Sidewall Angle at SiC Etch for Metal Filling Process, ***H.K. Sung***, *W.S. Lim, K.W. Lee, S.K. Kim, J.W. Choi, B.O. Lee, H.M. Yoon, Y.S. Lee, M.L. Park, E.A. Cho, J.K. Kim, H.K. Kang, C.G. Ko*, Korea Advanced Nano Fab Center, Republic of Korea

This study relates generally to etching processes and in particular to method for controlling the profile of an opening etched in a SiC wafer. In the fabrication of high power device via hole is formed in an insulating layer prior to metallization to provide contacts to underlying regions. It is preferable that these openings have a low slope etch profile in order to minimize the possibility of defects in the overlying metal layer. One problem is a step-coverage defect, which sometimes occurs when a metal layer is formed over an opening having a steep profile and causes a discontinuity in the conductor formed by the metal layer. Such steep openings, that is, openings having nearly vertical sidewalls, typically occur when an SiC wafer is anisotropically etched, for example by a etch mask of high selectivity metal.

In this study, the SiC etching chatacteristics and the dry etch mechanism of SiC as function of etch mask material(metal masks) and etch mask edge shape were investigated. The etched step height was measured using step profilometer. And Scanning Electron Microscope (SEM) was used to measure the etch profile. Also, X-ray Photoelectron spectroscopy (XPS) was utilized to analyze the SiC etch mechanism.

PS-ThP24 Etching Characteristics of Magnetic Tunnel Junction Layer by using Non-Corrossive Gas Mixtures in ICP System, ***M.H. Jeon**, K.N. Kim, H.J. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Magnetic random access memory (MRAM) has made a prominent progress in memory performance and has brought a bright prospect for the next generation nonvolatile memory technologies due to its several advantages. Dry etching process of magnetic thin film is one of the important issues for the magnetic devices such as magnetic tunneling junctions (MTJs) based MRAM. MTJs which are the basic elements of MRAM can be used as bits for information storage. CoFeB is a well-known soft ferromagnetic material, of particular interest for magnetic tunnel junctions (MTJs) and other devices based on tunneling magneto-resistance (TMR), such as spintransfer-torque MRAM. Recently, transferring the pattern by using an Ar+ ion milling is a commonly used, although the redeposition of sputter etch products on the sidewalls and the low etch rate are main disadvantages of this method. Other method, which reported the etch rates higher than 50 Å/s for magnetic multilayer structures using Cl_2/Ar plasmas, is also proposed. However, the chlorinated etch residues on the sidewalls of the etched features tend to severely corrode the magnetic material. To remove this problem, the etching of MTJ layer by using organic-based gases such as CO/NH_3, CH_3OH, etc. are actively investigated currently.

In this study, MTJ materials such as CoFeB, MgO, etc. were etched using various gas ratios which can be expected to form volatile metal-organic compounds and the results were compared with those etched using Cl_2-based gas mixture. As one of the gas mixtures, gas mixtures of carbon monoxide (CO) and ammonia (NH_3) were used as etching gases to form carbonyl volatiles. The etch results showed the enhanced etch rates higher than 3 times by using a gas mixture of CO/NH_3 compared to that etched by pure CO or NH_3 possibly indicating the formation of products composed of carbonyl volatiles. The composition of etched surface was less damaged compared with that etched with Cl_2-based gas.

PS-ThP25 Evaluation of Surface Chemical Bonding State and Surface Roughness of Chemical Dry Etched Si using NO and F_2 Gas Mixture, ***S. Tajima**, T. Hayashi, K. Ishikawa, M. Sekine, M. Hori*, Nagoya University, Japan

Economical Si etching is required to fabricate through silicon via (TSV) integration architecture for multi-layered packaging, micro-electro-mechanical system (MEMS), and surface patterning of solar panels. Chemical dry etching techniques by highly reactive ClF_3 gas [Ibbotson et al. J. Appl. Phys. 56 (1984) 2939] has been reported but the contamination by Cl is problematic. In this study, we have been investigating a new and economical Si chemical dry etching technique using nitric oxide (NO) and molecular fluorine (F_2) gas mixture. Atomic fluorine (F) is generated by mixing these gases at room temperature by the reaction of F_2 + NO à FNO + F. Kinetic energy of F at 0.8 eV and the change in post-reaction bonding energies of Si, SiF_x (x = 1~4), Si-NO, Si-NOF, and HF were calculated by B3LYP/6-311+G(d) in Gaussian 09. Si etch rate, etch directionality, etch selectivity, surface chemical bonding states, and surface roughness were evaluated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy, and atomic force microscopy to elucidate the Si etch dynamics in molecular level.

A prototype etching reactor was fabricated using the quartz tube with the inner diameter of 7.5 mm and the length of 150 mm. Flow rate of gases introduced into this chamber was Ar/5%F_2 ~ 38.5 sccm, F_2 ~ 1.9 sccm and NO ~ 1.5-5 sccm while maintaining the constant pressure at 620 Pa. The corresponding flow rate ratio, NO/NO + F_2, was 0.44 ~ 0.72. Etching was performed for 15 ~ 600 s. Single crystal and poly-Si samples were prepared to determine the etch rate, which is calculated from the cross-sectional SEM images. Preliminary results show that the etch rate was increased from 0.2 ~ 1.8 m m/min at NO/NO + F_2 = 0.44 ~ 0.72. This measured etch rate was more than 100 times faster than the estimated value by F atom reaction with H terminated Si. The etch rate sharply increased with NO up to NO/NO + F_2 ~0.57 and became almost constant when NO/NO + F_2 > 0.57. The etched surface after the exposure to the atmosphere mainly consisted of SiO_2, indicating that the reaction between Si-F_x, Si-NO, Si-NOF and H_2O in the air may occur rapidly. The detail analysis of the change in surface chemical bonding state during and after etching is in progress. The etched surface became rough and scalloped Si was formed when NO flow rate was increased. The surface roughening may be due to the presence of Si-NO and/or Si-NOF bond prior to the formation of Si-F_x that would eventually form SiF_4. From these results, Si etching is initiated not only the presence of F but also the existence of F_2, NO, and FNO.

PS-ThP26 High K Metal Gate Etching towards sub 14 nm Features, *S. Barnola, **L. Desvoivres**, C. Vizioz,* CEA, LETI, MINATEC Campus, France, *C. Arvet*, ST Microelectronics, Crolles, France

To progress towards the 11nm node, sub 14nm HK metal gates need to be patterned with a good CD control. Two lithography techniques were used at the same time on the wafer to achieve the same CD target for different goals : electron-Beam lithography with 30nm dense litho features for the circuit development and optical lithography with 80nm isolated features for single device optimization. A gate etching process has been developed at LETI starting from these two lithography options using different trimming strategies to achieve this aggressive CD target For this study, wafers were patterned with hybrid lithography. In the same die, E-beam and optical fields were realized separately using a common stack made of trilayer / hard masks/ HKMG. The optical side was first printed and patterned down to the Poly-si , then the ebeam side was printed with positive photoresist and etched to the Poly-Si as well. Finally the HKMG parts were etched at the same time on both fields.Metal Gate patterning has been performed in a 300mm industrial platform etcher: LAM VERSYS, Kiyo CX. Several conditions were tested to minimize added LWR for such small dimensions. We focused on several trimming conditions at different location on the stack to achieve our CD target : resist, ARC, SOC and hard mask. After optimization sub 14nm CD have been successfully achieved for FDSOI technology. Best results were achieved with hard mask trimming strategies for ebeam part and resist + hard mask trimming for optical part.

PS-ThP27 The SiO_x Thin Film Deposition by using a Double Discharge System with a HMDS/Ar/He/O_2 Gas Composition, ***G.Y. Kim**, J.B. Park, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Silicon oxide thin films have been extensively investigated due to the outstanding chracteristics such as hardness, specific chemical structure, and high scratch resistance. In most of cases, SiOx thin films are deposited by the plasma enhanced chemical vapor deposition processes because the high quality materials can be obtained. However, the PECVD has some drawbacks that are related to vacuum system. Therefore, plasma deposition at atmospheric pressure has received attention as promising technology. Among the many kinds of AP-plasma sources, Dielectric Barrier Discharge(DBD) source which consists of two parallel electrodes can get the uniform and large-area glow discharge. Especially, double discharge system which composed of direct-type DBD and remote-type DBD was improved the various mechanical characteristics of SiOx thin film and increased the process efficiency.In this paper, SiOx thin films with a low content of impurities were deposited by using a double discharge system with a gas mixture of hexamethyldisilazane (HMDS)/ O_2/ He/ Ar. The use of the double discharge system increased not only the SiOx thin film deposition rates, but also preocess efficiency. When AC voltage was applied to the remote-type DBD from 4 to 7 kV, the deposition rate of SiOx was increased from 7 to 36.1 nm/scan. Also as using double discharge system (5 kV, 20 kHz AC voltage was applied to the direct-type DBD), the deposition rate of the SiOx thin films was futher increased from 20 to 58.3 nm/scan with the increase of the AC biasing to the remote-type DBD from 4 to 7 kV. The improvment in the properties of SiOx films was partially related to the increased gas dissociation by the additional AC biasing of substrate.

PS-ThP28 The Effect of a Low Plasma-Induced Damage Etching on sub-32nm Metal Gate/High-*k* Dielectric CMOSFETs Characteristics, ***K.S. Min**, S.H. Kang, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

According to international technology roadmap for semiconductors (ITRS), as the critical dimension (CD) of metal-oxide-semiconductor field effect transistor (MOSFET) is scaled down to 45nm node and below, the present gate (poly-Si) with a high-k dielectric is intrinsically limited. Therefore, a metal gate compatible with a high-k dielectric, which is physically thicker with the same equivalent oxide thickness (EOT) has been investigated. For the etching of metal gate/high-k dielectric, reactive ion etching technique is currently applied to maintain accurate CD by etching the gate structure anisotropically with minimal damage on substrate. However, it can introduce plasma induced damages (PIDs) and was found to degrade the electric characteristics of metal gate/high-k dielectric CMOSFETs, particularly in the short channel devices. For low standby power (LSTP) application, an etch technique with low plasma-induced damage composed of neutral beam etching and atomic layer etching has been applied to metal gate and high-k dielectric etching of complementary metal-oxide-semiconductor field effect transistors (CMOSFETs), respectively, and their electrical characteristics were compared with those etched by conventional wet and dry etching techniques. It has been found that, after the etching using the low plasma-induced damaged etching technique, device performances have been improved compared to those etched by conventional wet and dry etching techniques. Especially, gate induced drain leakage and I_{off} which are key factors for LSTP have been reduced significantly.

PS-ThP29 Catalytic Activities of Metal/Carbon Compound used by Vacuum and Solution Plasma Processes, ***H.S. Lee***, *M.A. Bratescu, N. Saito*, Nagoya University, Japan

Fuel cells have been recognized as a potential clean energy-converting device due to their high efficiency and low emissions. However, two major technical gaps limit their commercializations: cost and reliability. Currently, platinum (Pt)-based catalysts and their corresponding cathode catalyst layers are among the major causes which limit their performance and cost for proton exchange membrane (PEM) fuel cells, although these are the most promising and practical fuel cell catalysts. Some approaches have been studied to reduce the cost and to improve the performance over twenty years, but there has been no real breakthrough yet. Recently, most researchers focused on the use of carbon catalyst and non-rare metal catalyst for replacement of Pt-based catalysts. The former groups are divided in organic dope methods and inorganic dope methods on carbon material such as nanotubes or graphene sheets. The major drawback of organic and inorganic dope method are, respectively, low thermal stability and limited controlling of the process. Meanwhile, non-rare metal catalysts show low catalytic activities.

In this study, we synthesized nickel/carbon nano-particles produced by solution plasma process.

SPP is a useful and simple method for the metal NPs synthesis because this non-equilibrium plasma can provide extremely rapid reactions due to the reactive chemical species, radicals and UV radiation produced in atmospheric pressure plasma operating in glow discharge limits and offering a suitable medium to control the chemical reactions inside the solutions.

The SPP was generated by the electrical discharge between opposite nickel electrodes. The glow discharge in 0.1 M KCl solution was produced by using bipolar pulsed power supply operated at 1~2 kV of voltage, 15 kHz of pulse frequency and 2 μs of pulse width. The diameter of the electrode was 0.6 mm and the interelectrode gap was 0.5 mm. In addition, 0.1 g of dispersion treated carbon (CNT, CNB) was inserted in 100 ml solution.

M/C NPs morphology was investigated by transmission electron microscopy, energy disperse X-ray microanalysis, X-ray Diffraction, Fourier transform infrared spectroscopy. Cyclic voltammetry was demonstrated for evaluating catalytic activities.

In conclusion, as applied voltage increased, diameter of synthesized NPs decreased. The smallest synthesized NPs with 3 nm showed the higher oxygen reduction rate in catalytic activities according to decrease diameter.

PS-ThP31 Plasma Etching of PTFE: Differences between Low and Atmospheric Pressure Treatments, ***N. Vandencasteele***, *J. Hubert, T. Dufour, S. Collette, C. De Vos, F. Reniers*, Université Libre de Bruxelles, Belgium

PTFE samples were treated by O_2/He plasma at various pressures, from low (6.67 Pa) to atmospheric pressure. Treatments were carried out using different mixtures of He and O_2. The first results highlight two completely different etching mechanisms depending on the gas mixture used and working pressure.

The etching was studied by mass loss measurements, weighing the sample before and after plasma exposure.

At low pressure the strongest etching occurs for pure oxygen plasma while no etching is detected for helium plasma. The opposite is observed at atmospheric pressure, the strongest etching takes place with pure helium.

X-ray photoelectron spectroscopy (XPS) analysis was used to study the chemistry of the PTFE surfaces as well as the etching products. High resolution F1s and C1s peak show different etching products as the pressure and/or the gas composition are changed. In all cases both carbon and fluorine are detected. Depending on the plasma parameters (pressure and gas composition) either CF_2 fragments (BE C1s = 292 eV) or CC (BE C1s = 285 eV) are detected.

Optical emission spectroscopy (OES) measurements were used to study the plasma phase and the etching products. A change in the He plasma emission was observed above a certain pressure (around 13.3 Pa). The plasma color changes from greenish to pink. This change could be related to the increase of the He metastable emission line at 389 nm. OES measurements also allowed us to detect etching products in the gas phase during the plasma exposure of the PTFE samples. Fluorine, CO and CO_2 lines were detected.

Those various results allow us to suggest two different mechanisms of PTFE etching.

In the case of low pressure O_2 plasma, the surface composition after the treatment and the etching products (detected by XPS and OES) suggest an etching mechanism where the C-F bonds are broken by charged particles (probably e^-). Oxygen then reacts with the carbon backbone to produce CO_2. The role of the charged particles was evidenced using different sample positioning and magnets.

In the case of atmospheric pressure treatments the etching occurs via the removal of CF_2 fragments. The main active specie responsible for the etching seems to be metastable He atoms.

PS-ThP32 Surface Modification of Polyethylene Terephthalate using Water Containing He/O_2 and Ar/O_2 Plasma, ***P. Leroy***, *S. Abou Rich, S. Colette, F. Reniers*, ULB, Belgium

Like many polymers, *Polyethylene Terephthalate (PET)* has excellent bulk physical and chemical properties but exhibit poor adhesion abilities. Therefore, in order to improve the deposition of a subsequent layer onto such compounds, a pretreatment of the surface is usually performed. Plasma treatments have a lot of advantages compared with other methods used to treat and modify such polymers like chemical, thermal or mechanical processes. Indeed the modifications only affect the top layer of the material without changing the bulk properties and it is environmental friendly (solvent free). *It is well known that plasma treatment improves the wettability and the hydrophilicity of polymers by surface oxydation,* creating at the interface new oxygen-based functionalities such as hydroxyl or carboxylic acid groups.

In this work, plasma treatment was performed on Polyethylene terephthalate (PET) using a Dielectric Barrier Discharge in Helium/ Oxygen and Argon/Oxygen mixtures at atmospheric pressure, and containing various concentration of water vapour. The experimental set up uses a roll-to-roll system, the film passing through electrodes at varying speeds (0.01m/min and 0.1m/min which correspond to film exposure times of 0.1 and 10 seconds respectively).

The goal of this work is to evaluate the influence of water vapour injection into the discharge on the polymer functionnalisation. It is shown that water changes the plasma characteristics, and strongly modifies the oxidative properties of the plasma. The influence of the water vapour partial pressure, the gap between electrodes and the power of the discharges are emphasized in order to optimize the surface wettability.

Chemical and physical changes on the polymer surface plasma treated are observed using X-ray Photoelectron Spectroscopy (XPS), Water Contact Angle and Atomic Force Microscopy (AFM) measurements.

PS-ThP33 Numerical Investigation of Optimum Conditions for Magnetic Neutral Loop Discharge Plasma Production, ***S.H. Kim***, *D. Akbar, J.L. Shohet,* University of Wisconsin-Madison*, B.N. Moon, W.J. Choi, Y.M. Sung*, Kyungsung University, Korea

In processing plasma sources for semiconductor device fabrication, both uniformity over a large area and controllability to obtain desirable plasma parameters are required. A magnetic neutral loop discharge (NLD) plasma[1] has been proposed as a new plasma source which satisfies these requirements. The position and the diameter of the plasma can be easily controlled by changing the position and the diameter of a neutral loop (NL). It has been theoretically shown that the electron motion becomes nonlinear around the NL when the radio frequency (RF) electric field is applied along the NL perpendicular to the magnetic field lines[2]. The electron makes meandering motions and acquires kinetic energy of several tens of electron-volts from the RF electric field where the meandering range contains the region between the NL and the electron cyclotron resonance (ECR) region, the length of which is designated by L[3,4]. Through such a process, the electrons are heated efficiently without collisions. The electron behavior near the NL determines the uniqueness of this plasma production technique and therefore details of its motion are needed. In this work, in order to accurately understand the characteristics of an NLD plasma, a numerical analysis of electron behavior around the NL was performed based on a 2-dimensional model in which three-dimensional effects were taken into account. For obtaining the optimum conditions for plasma production, the relationship between the normalized electric field and the average electron energy were also investigated.

This Work was supported by Kyungsung University Research Program (2011) and by the Semiconductor Research Corporation under Contact No. 2008-KJ-1871 and the National Science Foundation under Grant CBET-1066231.

[1] Z. Yoshida and T. Uchida., Jpn. J. Appl. Phys. **34** (1995) 4213.

[2] Z. Yoshida et al., Phys. Rev. Lett. **81** (1998) 2458.

[3] Y. M. Sung et al., J. Vac. Sci. Technol. **A18** (2000) 2149.

[4] Y. M. Sung et al., J. Vac. Sci. Technol. **B20** (2002) 1457.

PS-ThP34 No- Residue and High- Rate Etching of InGaAs by High Density Plasma, ***Y. Ohsawa***, Tokyo Electron Technology Center, America, LLC, *H. Nakajima, T. Nishizuka, M. Takahashi,* Tokyo Electron America, *Y. Trickett, G. Nakamura, A. Ko,* Tokyo Electron Technology Center, America, LLC, *H. Ohtake,* Tokyo Electron Technology Development Institute, INC., Japan, *C. Huffman, R. Hill*, SEMATECH

III-V materials are promising candidates for the channel materials beyond 10 nm generation of CMOS-logic devices. Among them, InGaAs was one of the best materials for NFET channel because of the high electron mobility. However, there are few reports of InGaAs etching. Previous reports showed that the problems were the residue of Indium and low etching rate. Because these issues came from the low reaction between the InGaAs surface and radicals, we have to enhance the surface reaction.In this paper, the precise InGaAs etching was investigated by high electron density (high Ne)/ low electron temperature (low Te) plasma with hot stage operation to improve the issue of residue and low rate. We used RLSA™ Etch tool as an InGaAs etcher. This tool has high Ne of more than 1×10^{11}cm^{-3} and low Te of less than 1 eV around the stage because RLSA™ Etch tool uses the surface wave plasma and diffusion chamber. A selection of gas chemistry and temperature was optimized to enable the proper plasma reactivity with Indium without creating residues. High rate of more than 100nm/ min was obtained without Indium residue. Since the reaction of Indium- methyl radical are enhanced by more than 150 ºC, it was considered that the etching reaction was enhanced by hot stage. In addition, the re-deposition of by-products was reduced because of low electron temperature. Based on additional analytical investigations, we found that the combination of high Ne- low Te plasma and hot stage is one of the best solution for no-residue and high rate etching of InGaAs.

PS-ThP35 Using Capillary Array Windows to Minimize Ion Bombardment Effects during Plasma Processing of Dielectrics, ***K.W. Hsu***, *F.A. Choudhury, H. Ren,* University of Wisconsin-Madison, *B.N. Moon,* Kyungsung University, Korea, *A.G. Olson,* University of Wisconsin-Madison, *Y.M. Sung,* Kyungsung University, Korea, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Microelectronic devices are often exposed to radiation and charged-particle bombardment from processing plasmas during their fabrication stages often resulting in damage to the dielectric materials. This work investigates the effectiveness of capillary-array windows to partially block charged particles in order to distinguish the effects of photons and charged particle bombardment during plasma exposure. A capillary-array window is placed over a 1×1 cm2 exposed area of an aluminum wafer chuck [i] in an ECR reactor and the substrate current during plasma exposure is measured at different bias voltages with and without the capillary window in order to determine the effectiveness of the window to partially block charged particles. Additionally, using an Object-Oriented-Particle-in-cell (OOPIC) code [ii], the ion and electron fluxes passing through the window can be estimated. The experimental measurements and the simulation results confirm that the capillary-array window can be arranged to block almost all ions during plasma exposure.

This work has been supported by Semiconductor Research Corporation under Contact No. 2008-KJ-1871 and the National Science Foundation under Grant CBET-1066231.

[i] T. Lucatorto, T. J. Mcllrath, and J. R. Roberts, *Appl. Opt*. **18**, 2505 (1979)

[ii]Y. M. Sung, M. Wada, M. Otsubo, C. Honda, Y. K. Kim, and C. H., *J. Appl. Phys*. **43** 800 (2004)

PS-ThP36 Deposition of YSZ Thin Films by Laser-Assisted Plasma Coating at Atmospheric Pressure (LAPCAP), ***Z. Ouyang***, *Y.L. Wu, P. Raman, L. Meng, T.S. Cho, D.N. Ruzic*, University of Illinois at Urbana Champaign

A laser-assisted plasma-coating technique at atmospheric pressure (LAPCAP) for depositing thin yttria-stabilized-zirconia (YSZ) films has been developed. This technique allows columnar-structured YSZ films with a thickness of 1~5 µm to be prepared on a Ni-based superalloy substrate at atmospheric pressure. The atmospheric pressure plasma is generated in a microwave-induced plasma torch system with a gas temperature T_g of more than 2,000 °C. Optical emission spectroscopy (OES) technique has been used to spatially analyze some critical characteristics of plasma, such as electron density ($n_e > 10^{15}$ cm^{-3}), electron temperature ($T_e \sim 1$ eV), and plasma gas temperature ($T_g \sim$ 800-1200 °C). The thermally grown oxide (TGO) layer is found to affect the film morphology significantly, and characteristics of TGO grown by pre-heating the substrate to 800-1200 °C are investigated. TGO in the form of α-Al_2O_3 with a thickness of ~ 1 µm is found to provide a means to deposit high quality, adhesive thin YSZ films on substrates with columnar microstructure, same as seen in films by high-vacuum electron-beam PVD method. The morphology and characteristics of the films have been compared at various deposition temperatures (100-1200 ºC) and laser energy density (1-10 J/cm^2), using microanalysis techniques such as scanning electron microscope (SEM), focused ion beam (FIB), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

PS-ThP38 Plasma Propagation Speed and Electron Temperature in Atmospheric Pressure Non-thermal Bioplasma Jet, ***P. Suanpoot,*** Maejo University Phrae Campus, Thailand, *Y.G. Han, W.Y. Lee, G.S. Cho, E.H. Choi*, Kwangwoon University, Republic of Korea

Space and time resolved discharge images from an atmospheric pressure non-thermal bioplasma jet have been observed by a high-speed single-frame camera to investigate the electron temperatures. The plasma propagation speed on the cathode has been shown to be about 5 km/s at input voltage of 4.7 kV and driving frequency of 40 kHz. Particularly, the electron temperature in atmospheric pressure non-thermal bioplasma jet were found to be about 1.5 eV at input voltage of 4.7 kV and driving frequency of 40 kHz, respectively. Implications of the results and directions for further studies are discussed. **Key words :** Non-thermal plasma jet, Plasma propagation speed, Electron temperature ______________ # This project is supported by Kwangwoon University Research Fund, Korea .

PS-ThP39 Increase Film Quality and Campaign Length in Reactive Sputtering Applications With Pulsed-DC Power, ***D. Pelleymounter***, Advanced Energy Industries Inc.

In reactive sputtering applications, arcs can contribute to costly film defects and process interruptions. Charge buildups on small areas of the target cause these electrical breakdowns, or arcs, which manifest as particles on the substrate—leading to defects, pinholes, rate reduction, short circuits, or other undesirable process disturbances and loss of film quality. Entire lots are oftentimes scrapped due to poor quality thin film layers, and severe arcing can damage equipment and shut down entire lines for maintenance. While there are several types of process power technologies available to help manage arcs, pulsed-DC technology offers a marked performance advantage over AC or straight DC power. The addition of low frequency pulsing lowers the effective electronic voltage of the whole plasma while maintaining the actual delivered voltage of individual electrons for high deposition rate and film flatness. Improved packing density also results. Adding reverse voltage while pulsing momentarily stops the energized electrons in the plasma and creates a haphazard path to the substrate, preventing hills and valleys from forming. This paper discusses how pulsed DC power conversion technologies can do much more than supply power but effectively manage arcs for greater surface control, film quality, and overall process control.

PS-ThP40 Control of Radical/Ion Ratios in Electron Beam-Generated Plasmas and their Effect on Polymer Surface Modification, ***S.G. Walton***, *E.H. Lock, R. Fernsler*, Naval Research Laboratory

Electron beam-generated plasmas are unique type of plasmas generated when high electron energy beam is injected into the gas. The beam preferentially ionizes the gas molecules, thereby producing daughter electrons with energies up to half of the initial beam energy. The daughter electrons, however, quickly lose energy as they collide with gas molecules. Thus, without an external electric field to heat them, the daughter electrons cool and they soon outnumber the beam electrons and the energetic daughter electrons responsible for ionization. The low-energy "plasma" electrons are not only far more populous, but also largely determine the plasma characteristics – i.e. the plasma density n_e, plasma potential f_p, and electron temperature $T_{e.}$ Typically T_e is 1 eV or less in beam-produced plasmas and thus the kinetic energy of the ions bombarding the surface is below the polymer bond energies. In this talk we estimate the charged, excited and resonant species concentrations and the fluxes bombarding the polymer surface. We correlate the ion to radical ratios in different gas environments with observed morphological and chemical modifications in polystyrene, poly(methyl methacrylate) and polyethylene. This work was supported by Naval Research Laboratory Base Program.

PS-ThP43 Atomic Layer Etching of Ultra-thin High-k Dielectric Film for Gate Oxide in MOSFET Devices, ***C.K. Kim***, Sungkyunkwan University, Republic of Korea, *J.K. Kim,* Samsung Electronics Co. Ltd., Republic of Korea, *G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

As the dimensions of integrated circuit devices, such as metal-oxide-semiconductor field effect transistors (MOSFETs), etc., continue to be scaled down, the thickness of gate dielectrics, such as SiO_2, etc., also continues to be scaled down to nanosize. Tunneling currents through the

gate dielectric, however, limit the scaling of SiO_2 to approximately a few nanometers. Therefore, for further scaling down of devices, alternate gate dielectric materials with higher dielectric constants need to be used to reduce the gate leakage current while maintaining the gate dielectric capacitance with a thicker material. Considerable research attention has focused on the potential of HfO_2 as a next generation gate dielectric material due to many advantages in comparison with SiO_2, such as a high dielectric constant (15–25), good thermal stability, wide band gap (5.6 eV) and large band offsets (1.5 eV). However, conventional RIE of ultra-thin HfO_2 film tends to cause electrical and physical damage to the surface of the devices due to use of energetic reactive ions and the difficulty in the precise etch rate (depth) control at an atomic scale. Precise etch depth control of ultra-thin HfO_2 (3.5 nm) films applied as a gate oxide material was investigated by using atomic layer etching (ALET) with an energetic Ar neutral beam and BCl_3 gas to minimize etch damage. A monolayer etching condition of 1.2 Å/cycle with a low surface roughness and an unchanged surface composition was observed for ultra-thin, ALET-etched HfO_2 by supplying BCl_3 gas and an Ar neutral beam at higher levels than the critical pressure and dose, respectively. When HfO_2-nMOSFET devices were fabricated by ALET, a 70% increase in the drain current and a lower leakage current were observed compared with the device fabricated by conventional reactive ion etching, which was attributed to the decreased structural and electrical damage.

PS-ThP44 Study on the Plasma Damage on the Interface between the Titanium Nitride and Hafnium Oxide during Etching Carbon Mask on the Titanium Nitride*, K.H. Bai,* ***Y. Jeon****, M.C. Kim, S. Choi*, Samsung Electronics Co. Ltd., Republic of Korea

We investigated the etch damage on the interface between the titanium nitride(TiN) and hafnium oxide(HfO2) during etching the carbon layer on the TiN. HfO2 is widely used as a high-k gate dielectric material to reduce the gate leakage current and improve the reliability in the semiconductor device. TiN and amorphous carbon layer(ACL) are deposited on the HfO2 as a gate electrode and mask material, respectably. We fabricated complimentary metal oxide semiconductor (CMOS) devices with patterning ACL on the TiN by dry etching and removing the TiN layer by wet chemical. We realized that an interlayer between the TiN and HfO2 layer was generated due to the plasma damage during the ACL etching and the interlayer was not removed clearly by the wet chemical, which resulted in device degradations. We studied the properties of the interlayer with changing the ACL etching recipe to find the key factor of generating the interlayer. The properties changed significantly with the ion energy and the gas composition of the ACL etch recipe.

PS-ThP45 Experimental and Simulation Studies of Capacitively Coupled Silan-Hydrogen Plasmas for Deposition of m-C Si Film*,* ***C.-H. Fan****, S.-E. Lien, K.-C. Leou,* National Tsing Hua University, Taiwan, Republic of China*, C.-H. Hsieh, M.-C. Wang, C.-F. Ai*, Institute of Nuclear Energy Research, Taiwan, Republic of China

Capacitively coupled SiH_4/H_2 plasmas (CCP) have benn widely employed for depostion of Si film for applications such as thin film transistors and thin film solar cells. For Si thin film solar cells, requirements for yielding higher vonversion efficiency at a lower cost calls for a high rate and high uniformity plasma porcess for deposition of microcrystalline Si film. A better understanding of the plasma discharge is needed. In this study, a VHF SiH_4/H_2 CCP discharge has been investigated by both numerical simulation, based on fluid model, and experimental study employing plasma optical emission spectroscopy analysis. Simulation was performed for VHF SiH_4/H_2 CCP operated at 27.12 MHz with 27 species and 47 reactions. Simulation results show that, for a power density of 0.4 W/cm^2, a gas pressure of 600 Pa and a SiH_4/H_2 flow rate ratio, or hydrogen dilution ratio, of 2.5/200, electron density profile is quite unifrom in the discharge region with a plasma desity up to $1.8X10^{16}$ m^{-3}. For the key species related to the film growth, i.e., SiH_3 and H, the densities of their fluxes arriving on the grounded substrate surface are uniform. Their ratio, which controls the crystaline fraction of the Si film, is strongly dependent on plasma parameters, such as rf power, hydrogen dilution dilution ratio and gas pressure. Results from experimental OES analysis show similar trends as predicted by the simulation as rf power and hydrogen dilution ratio were varied but little correlation was found as gas pressure was changed. The discrepency, however, can be explained by analyzing the reactions responsible for the production and loss of SiH_3 and SiH_2. The detailed results from simulation and OES analysis of the parametric analysis ob varying, rf power, gas flow rates and gas pressures will be presented.

*Work supported by the National Science Council of ROC.

PS-ThP46 Diagnostic Study of Plasmas in Solution Driven by Pulsed Power - Study of History Effect and Observation of S_2 Emission*,* ***C.Y. Sie****, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Diagnostic studies of plasmas in salt solutions are performed. The plasma is sustained by a pulse power source with the pulse voltage up to 600 V, T_{on} (voltage on duration) between 10 µs to 1 s, and T_{off} (voltage off duration) between 30 µs to 3 s. The driving electrode is made of a platinum wire with a diameter of 0.5 mm covered by a glass tube to precisely define the area in contact with the solution. The grounding electrode is a bare platinum wire with the same diameter with a length of approximately 1 cm. The power electrode is set upward and both electrodes are immersed in salt solution. Current and voltage probes are used to monitor the current and voltage waveforms, respectively. An optical emission spectrometer is used to monitor the emission spectra generated by the plasma. In the first part, we demonstrate the observation of the history effect. With a sufficiently short T_{off} (less than 100 ms), the history effect, i.e. the plasma generated in one power cycle is consistently affected by that generated in the previously cycle, is observed when $NaNO_3$ solution are used. With the history effect, the maximum current within a power cycle increases with cycles, from the first cycle upon Ton. With a sufficiently long T_{off} (~2 s), good cycle to cycle reproducibility is observed, and the current waveform in each cycle is nearly identical. The history effect is therefore fully eliminated. The transition characteristic time is 0.1 to 1 s, which suggests heating of the electrode is the major mechanism for the history effect. In the second part, we show the detection of S_2 emission when the plasma is ignited in low concentration Na_2SO_4. The intensity of S_2 emission gradually drops to the noise level with a long operating time. This observation suggests that the optical emission emanating from the plasma involves a more complex pathway than those suggested in the literature.

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Baldwin, M.J.: PS2-WeA1, 32
Banik, A.: PS2-TuM1, 13; PS2-TuM6, 14
Banna, S.: PS-ThA10, 40
Barankova, H.: SE+PS-TuA7, **21**
Bardos, L.: SE+PS-TuA7, 21
Barker, P.M.: SE+PS-TuM5, 16
Barnola, S.: PS2-TuM5, **14**; PS-ThP26, 45
Barraud, S.: PS2-TuM5, 14
Bartis, E.: PS+BI-MoA2, 8; PS+BI-MoA6, **8**
Barton, D.: EL+TF+AS+EM+SS+PS+EN+NM-MoM10, 2
Batan, A.: SE+PS-TuA9, 22
Beard, M.: PS2-TuM9, 14; PS-ThP1, 41; PS-WeM1, 28
Becker, J.S.: PS1-TuA11, 18
Bedzyk, M.J.: GR+AS+BI+PS+SS-WeM1, **25**
Bekman, H.H.P.Th.: PS-ThP15, 43
Bennett, C.J.: GR+AS+BI+PS+SS-WeM9, 26
Besnier, J.-F.: EL+TF+AS+EM+SS+PS+EN+NM-MoM3, 1
Bezares, F.J.: GR+AS+BI+PS+SS-WeM9, 26
Biolsi, P.: PS2-TuM1, 13; PS-MoM5, 6
Blanchet, P.: PS+BI-MoA11, 9
Blechle, J.M.: PS-ThP19, **44**
Bodart, P.: PS1-WeA2, 30
Bolt, R.J.: PS-ThA9, 40
Booth, J.-P.: EN+PS-WeM5, 23
Boris, D.R.: PS1-TuM12, **13**
Bouarouri, A.: PS+BI-MoA10, **9**
Boufnichel, M.: PS1-ThM3, 35
Braithwaite, N.St.: PS1-WeA2, 30
Bratescu, M.A.: PS-ThP29, 46
Bray, J.A.: PS-ThA10, 40
Brehmer, F.: EN+PS-WeM3, 23
Brigg, W.: PS2-MoA6, 10
Brihoum, M.: PS1-WeA2, 30; PS-ThP5, 41; PS-ThP7, 42
Brink, M.: PS1-ThM12, 36
Bronneberg, A.C.: PS2-WeA9, 33
Bruce, R.L.: PS-MoM6, 6; PS-WeM10, **29**
Byrns, B.: SE+PS-TuA3, **21**; SE+PS-TuA4, 21
Bystrov, K.: PS2-WeA1, 32

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Caldwell, J.D.: GR+AS+BI+PS+SS-WeM9, 26
Cao, J.: PS2-ThM5, 37
Carbone, E.A.D.: PS1-WeA7, 30
Cardinaud, C.: PS2-WeA10, 33
Carter, D.: PS-ThA4, **39**; PS-ThA6, 39
Chabal, Y.J.: GR+AS+BI+PS+SS-WeM2, 25
Chang, H.W.: PS+BI-MoA1, **8**
Chang, J.: PS2-TuM6, 14
Chang, J.P.: PS1-ThM11, 36; PS-MoM3, **6**
Chen, H.: PS2-TuM9, 14
Chen, J.: EL+TF+AS+EM+SS+PS+EN+NM-MoM4, 1; PS1-ThM11, 36
Chen, L.: PS1-TuM11, 13; PS1-WeA12, 31; PS2-MoA10, 11; PS2-MoA11, 11; PS2-MoA9, 11
Chen, Q.: PS+BI-MoA8, 9
Chen, S.: PS2-ThM5, 37
Chen, T.Q.: PS-WeM1, 28; PS-WeM11, 29
Chen, Z.: PS1-TuA10, **18**
Cheng, J.: PS1-ThM12, 36; PS-ThP10, 42
Chesaux, M.: PS-ThA3, **39**
Chiba, Y.: PS-ThP1, 41; PS-WeM4, 28
Chiou, P.W.: PS-ThP22, 44
Cho, E.A.: PS-ThP23, 44
Cho, G.S.: PS+BI-MoA3, 8; PS-ThP38, 47
Cho, T.S.: PS-ThP36, 47; SE+PS-TuM3, 15; SE+PS-TuM4, 15
Choi, D.H.: PS2-TuM6, 14
Choi, E.H.: PS+BI-MoA3, **8**; PS-ThP38, 47
Choi, J.: PS2-TuM11, 15
Choi, J.W.: PS-ThP23, 44
Choi, J.Y.: GR+EM+NS+PS+SS+TF-MoM11, 4
Choi, S.: PS-ThP44, 48
Choi, W.J.: PS-ThP33, 46
Chou, C.C.: PS-ThP22, 44
Choudhury, F.A.: PS-ThP35, 47
Chu, J.-W.: PS+BI-MoA2, 8; PS+BI-MoA6, 8
Chun, Y.S.: PS1-ThM6, **35**
Chung, T.-Y.: PS+BI-MoA2, **8**; PS+BI-MoA6, 8
Chyan, O.: PS-WeM5, **29**
Clark, K.: GR+EM+NS+PS+SS+TF-MoM2, 3
Clergereaux, R.: PS+BI-MoA10, 9
Coïa, C.: PS1-WeA9, 31
Colburn, M.: PS2-TuM9, 14
Colette, S.: PS-ThP32, 46
Collette, S.: PS-ThP31, 46
Collins, K.: PS2-MoA3, 10
Collins, R.W.: EL+TF+AS+EM+SS+PS+EN+NM-MoM1, **1**; EL+TF+AS+EM+SS+PS+EN+NM-MoM4, 1
Copel, M.W.: GR+EM+NS+PS+SS+TF-MoM8, 3
Cossement, D.: PS1-TuA8, 17
Côté, C.: PS+TC-WeM1, 26
Creatore, M.: EL+TF+AS+EM+SS+PS+EN+NM-MoM6, 2; PS1-TuA1, **17**; PS2-WeA9, 33
Cuddy, M.F.: PS2-WeA7, **32**; PS-ThP19, 44
Cui, J.B.: PS1-TuA12, 18
Culbertson, J.C.: GR+EM+NS+PS+SS+TF-MoM3, 3
Cunge, G.: PS1-WeA2, **30**; PS2-WeA12, 34; PS-ThP7, 42
Cuomo, J.: SE+PS-TuA3, 21
Czarnetzki, U.: EN+PS-WeM12, 24; EN+PS-WeM9, 24

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Daniels, S.: PS1-TuM3, 12; PS1-TuM9, 13; PS1-WeA1, 30
Darnon, M.: PS1-WeA2, 30
Darrell, J.W.: PS-ThP21, 44
Davydova, A.: PS2-WeA12, 34
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De Graeve, I.: SE+PS-TuA9, 22
de Marneffe, J.-F.: PS1-ThM2, 35
De Temmerman, G.: PS2-WeA1, **32**
De Vos, C.: PS-ThP31, 46
de Vries, H.: PS+TC-WeM2, 26
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Denis, L.: PS1-TuA8, 17
Desbief, S.: PS+TC-WeM11, 27
Despiau-Pujo, E.: PS1-WeA2, 30; PS2-WeA12, **34**
Desvoivres, L.: PS2-TuM5, 14; PS-ThP26, **45**
Diao, L.: PS2-TuM10, **15**
Diebold, A.C.: EL+TF+AS+EM+SS+PS+EN+NM-MoM9, **2**
Ding, G.: PS-ThP10, **42**
Diomede, P.: PS2-MoA1, **10**
Doerner, R.P.: PS2-WeA1, 32
Dogan, I.: EN+PS-WeM4, **23**
Dohnalova, K.: EN+PS-WeM4, 23
Dolinaj, B.: PS1-WeA1, **30**
Dominé, D.: PS-ThA3, 39
Donnelly, V.M.: PS1-TuA10, 18; PS2-MoA1, 10; PS2-TuA3, 19; PS2-WeA11, 33; PS-MoM8, 7; PS-ThP18, 44
Doris, B.: EL+TF+AS+EM+SS+PS+EN+NM-MoM9, 2
Dornstetter, J.-C.: EL+TF+AS+EM+SS+PS+EN+NM-MoM3, **1**
Dougherty, D.B.: GR+AS+BI+PS+SS-WeM10, 26
Dubois, P.: PS1-TuA8, 17
Dufour, T.: PS+TC-WeM11, 27; PS-ThP2, **41**; PS-ThP31, 46
Dussarrat, C.: PS-WeM3, 28
Dussart, R.: PS+EM-MoM3, **4**; PS1-ThM2, 35; PS1-ThM3, 35

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Economou, D.J.: PS1-TuA10, 18; PS2-MoA1, 10; PS2-WeA11, 33; PS-MoM8, 7; PS-ThP18, 44
Eddy, Jr., C.R.: GR+AS+BI+PS+SS-WeM9, 26; GR+EM+NS+PS+SS+TF-MoM1, 2; GR+EM+NS+PS+SS+TF-MoM3, 3
Eden, J.G.: PS+EM-MoM1, **4**
Elferink, F.H.: PS-ThP15, 43
Elliston, R.: PS2-TuM10, 15
Emery, J.D.: GR+AS+BI+PS+SS-WeM1, 25
Engelmann, S.: PS1-ThM12, 36; PS-MoM2, **6**; PS-WeM10, 29
Engeln, R.: EN+PS-WeM3, **23**; PS+TC-WeM2, 26
Enta, Y.: GR+EM+NS+PS+SS+TF-MoM10, 4
Eriguchi, K.: PS2-TuA10, 20; PS2-TuA12, 20; PS-MoM10, **7**
Exarhos, S.A.: PS-ThP21, **44**

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Fan, C.-H.: PS-ThP45, **48**
Fanelli, F.: PS+TC-WeM5, **27**
Farmer, B.L.: GR+AS+BI+PS+SS-WeM6, 25
Fauzi, M.E.: EN+PS-WeM11, **24**; PS2-ThM10, 38
Felix, V.: PS+EM-MoM3, 4
Fenter, P.: GR+AS+BI+PS+SS-WeM1, 25
Fernsler, R.: PS1-TuM12, 13; PS-ThP40, 47
Feurprier, Y.: PS-ThP1, 41; PS-WeM4, **28**
Fisher, E.R.: PS2-WeA7, 32; PS-ThP19, 44
Fouchier, M.: PS-ThP5, **41**; PS-ThP7, 42
Fox-Lyon, N.: PS2-WeA11, **33**
Fracassi, F.: PS+TC-WeM5, 27
Fradet, M.: PS1-WeA9, **31**
Franke, E.: PS-MoM1, 6
Franz, G.: PS1-WeA10, **31**
Franz, R.: SE+PS-TuM10, **16**
Friddle, P.: PS-MoM1, 6
Fromm, F.: GR+EM+NS+PS+SS+TF-MoM10, 4
Fukasawa, M.: PS2-ThM4, 37; PS2-TuA9, 20; PS-MoM10, 7; PS-ThP14, **43**
Fukidome, H.: GR+EM+NS+PS+SS+TF-MoM10, **4**
Fuller, N.C.M.: PS1-ThM12, 36; PS-MoM2, 6; PS-MoM6, 6; PS-WeM10, 29
Funk, M.: PS1-TuM11, 13; PS1-WeA12, **31**

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Gaddam, S.: PS2-WeA8, 33
Gahan, D.: PS1-WeA1, 30
Gaman, C.: PS1-TuM9, 13
Garces, N.Y.: GR+EM+NS+PS+SS+TF-MoM1, 2; GR+EM+NS+PS+SS+TF-MoM3, 3
Gaskill, D.K.: GR+AS+BI+PS+SS-WeM9, 26; GR+EM+NS+PS+SS+TF-MoM1, **2**; GR+EM+NS+PS+SS+TF-MoM3, 3
Gherardi, N.: PS+BI-MoA10, 9; PS+BI-MoA11, 9
Gizzo, V.: PS-ThP1, 41
Go, D.B.: PS+EM-MoM11, 6
Gottscho, R.: PS2-TuM3, 14
Graef, W.A.A.D.: PS1-WeA7, 30
Graham, W.S.: PS1-ThM12, 36; PS-MoM2, 6
Granier, A.: PS2-WeA10, 33
Grant, J.T.: SE+PS-TuM9, 16
Graves, D.B.: PS+BI-MoA2, 8; PS+BI-MoA6, 8; PS2-WeA11, 33; PS2-WeA12, 34; PS-WeM6, 29
Gregorkiewicz, T.: EN+PS-WeM4, 23
Griesser, H.J.: PS+BI-MoA7, 9; PS1-TuA3, 17
Griffin, T.M.: PS-ThA10, 40
Grilley, R.: PS-ThA4, 39
Gudimenko, E.: PS1-TuM3, **12**
Guillorn, M.A.: PS1-ThM12, 36
Gupta, R.: PS-WeM3, 28
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Haass, M.: PS1-WeA2, 30; PS-MoM6, 6
Hall, C.J.: PS1-TuA3, **17**
Hamaguchi, S.: PS1-ThM5, 35; PS2-TuA2, 19; PS2-TuA4, 19; PS2-TuA9, **20**; PS-ThP6, 42
Han, L.: EN+PS-WeM10, **24**
Han, Y.G.: PS-ThP38, 47
Handa, H.: GR+EM+NS+PS+SS+TF-MoM10, 4
Hannon, J.B.: GR+EM+NS+PS+SS+TF-MoM8, 3
Hartig, M.: PS2-TuM9, 14
Hatakeyama, R.: PS+BI-MoA8, 9
Hayashi, T.: PS2-MoA7, 11; PS-ThP25, 45
He, J.: PS2-TuM11, 15
Heo, D.: PS2-TuM11, 15
Hernández, S.C.: GR+AS+BI+PS+SS-WeM9, **26**; GR+EM+NS+PS+SS+TF-MoM1, 2
Hersam, M.C.: GR+AS+BI+PS+SS-WeM1, 25; GR+AS+BI+PS+SS-WeM3, **25**
Hershkowitz, N.: PS2-WeA4, 32
Hicks, R.F.: PS+EM-MoM9, 5
Hill, R.: PS-ThP34, 47
Hilpert, F.: PS2-TuA1, 19
Hirano, A.: SE+PS-TuA8, 22
Hirvonen, J.: PS+TC-WeM12, 28
Hoffman, D.: PS-ThA4, 39; PS-ThA6, 39
Holland, J.: PS-MoM11, 7
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Holohan, A.: PS1-TuM9, 13
Honda, M.: PS-ThP12, **43**
Honda, T.: PS-ThP14, 43
Hong, M.: PS2-ThM1, **36**
Hopkins, M.B.: PS1-WeA1, 30
Hopwood, J.: PS+EM-MoM5, **5**
Hori, M.: PS1-TuM5, 12; PS2-MoA7, 11; PS2-ThM5, 37; PS2-TuA7, 19; PS2-WeA3, 32; PS-ThP14, 43; PS-ThP25, 45
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Horie, T.: PS2-ThM3, 37
Horsfall, A.B.: GR+EM+NS+PS+SS+TF-MoM1, 2
Hoshino, K.: PS-ThP6, **42**
Hoskinson, A.: PS+EM-MoM5, 5
Howe, J.: GR+EM+NS+PS+SS+TF-MoM3, 3
Howling, A.A.: PS-ThA3, 39
Hsieh, C.-H.: PS-ThP45, 48
Hsu, C.C.: PS+BI-MoA1, 8; PS+EM-MoM4, 5; PS-ThP22, 44; PS-ThP46, 48
Hsu, K.W.: PS-ThP35, **47**
Hu, W.: EN+PS-WeM11, 24; PS2-ThM10, 38
Hua, X.: PS2-TuM11, 15
Hubert, J.: PS+TC-WeM11, **27**; PS-ThP2, 41; PS-ThP31, 46
Hübner, S.: PS1-WeA7, 30
Hudak, S.: SE+PS-TuA3, 21
Huffman, C.: PS-ThP34, 47
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Ide, T.: GR+EM+NS+PS+SS+TF-MoM10, 4
Igarashi, M.: EN+PS-WeM11, 24; PS2-ThM10, 38
Ikezawa, S.: PS1-WeA3, 30
Iliev, M.N.: PS1-TuA10, 18
Inada, A.: PS-MoM5, 6; PS-ThP1, 41
Iriye, Y.: PS2-ThM9, 37
Ishibashi, K.: PS2-MoA11, 11
Ishigami, M.: GR+AS+BI+PS+SS-WeM6, **25**
Ishikawa, K.: PS1-TuM5, 12; PS2-MoA7, 11; PS2-ThM5, 37; PS2-TuA7, **19**; PS2-WeA3, 32; PS-ThP14, 43; PS-ThP25, 45
Isobe, M.: PS2-TuA4, 19; PS2-TuA9, 20; PS-ThP6, 42
Ito, M.: PS2-TuA7, 19
Ito, T.: PS1-ThM5, 35; PS2-TuA2, **19**; PS2-TuA9, 20; PS-ThP6, 42
Itou, A.: PS-MoM2, 6; PS-WeM10, 29
Iwao, T.: PS2-MoA11, 11
Iwasaki, T.: PS2-ThM9, 37
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Izawa, M.: PS-ThA1, 39
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Jacq, S.: PS2-WeA10, 33
Jakubiak, R.: SE+PS-TuM9, 16
Jakubowski, A.: PS2-WeA3, 32
Jang, L.: PS2-TuM9, 14
Janssen, J.P.B.: PS-ThA9, 40
Jeon, M.H.: PS-ThP24, **45**
Jeon, Y.: PS-ThP44, **48**
Ji, S.-H.: GR+EM+NS+PS+SS+TF-MoM8, 3
Ji, X.: PS2-TuM11, 15
Johnson, C.W.: PS1-TuM4, 12
Johnson, D.J.: PS1-TuM4, 12
Johnson, E.V.: EN+PS-WeM5, **23**
Jones, J.G.: SE+PS-TuM9, 16
Joo, Y.H.: PS1-ThM6, 35
Joseph, E.A.: PS1-ThM12, 36; PS-MoM2, 6; PS-WeM10, 29
Joubert, O.: PS1-WeA2, 30; PS-ThP7, 42
Jung, R.: PS+BI-MoA3, 8; PS2-TuM1, 13; PS2-TuM6, 14; PS2-TuM9, 14; PS-MoM5, 6
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Kakaroglou, A.: SE+PS-TuA9, 22
Kakiuchi, H.: PS+TC-WeM3, 27; SE+PS-TuA8, **22**
Kamarthy, G.: PS-MoM1, 6; PS-MoM11, 7
Kambhampati, R.: PS2-TuM6, 14
Kanakasabapathy, S.: PS2-TuM1, 13; PS2-TuM6, 14; PS2-TuM9, 14; PS-MoM1, 6; PS-MoM5, 6
Kaneko, T.: PS+BI-MoA8, **9**
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Kang, X.: PS2-WeA9, 33
Kao, P.K.: PS-ThP22, **44**
Karahashi, K.: PS1-ThM5, **35**; PS2-TuA2, 19; PS2-TuA9, 20; PS-ThP6, 42
Karakas, E.: PS-ThP18, **44**
Kashimura, K.: PS2-ThM3, 37
Kasouit, S.: EL+TF+AS+EM+SS+PS+EN+NM-MoM3, 1
Katoch, J.: GR+AS+BI+PS+SS-WeM6, 25
Katsunuma, T.: PS-ThP12, 43
Kawai, Y.: GR+EM+NS+PS+SS+TF-MoM10, 4
Kazi, H.Ur.: PS2-WeA8, **33**
Kelber, J.A.: PS2-WeA8, 33
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Kessels, W.M.M.: EL+TF+AS+EM+SS+PS+EN+NM-MoM6, 2; PS2-WeA9, 33
Keville, B.J.: PS1-TuM10, **13**; PS1-TuM9, 13
Khan, A.: PS2-TuM11, 15
Khare, R.: PS2-TuA3, 19
Khrabrov, A.V.: PS2-MoA10, **11**; PS2-MoA9, 11
Kikuchi, Y.: PS1-TuA9, **18**
Kilicaslan, A.: PS+TC-WeM1, **26**
Kim, C.I.: PS1-ThM6, 35
Kim, C.K.: PS-ThP43, **47**
Kim, G.Y.: PS+TC-WeM9, 27; PS-ThP27, **45**
Kim, H.J.: PS-ThP24, 45
Kim, J.-H.: PS-ThP4, **41**
Kim, J.K.: PS-ThP23, 44; PS-ThP43, 47
Kim, K.N.: PS-ThP24, 45
Kim, M.C.: PS-ThP44, 48
Kim, S.H.: PS-ThP33, **46**
Kim, S.K.: PS-ThP23, 44
Kim, S.N.: GR+AS+BI+PS+SS-WeM6, 25
Kim, Y.: PS+BI-MoA3, 8
Kinoshita, K.: PS1-ThM9, **36**
Kinoshita, T.: GR+EM+NS+PS+SS+TF-MoM10, 4; PS2-ThM4, 37
Kintaka, H.: PS2-TuM1, 13; PS-MoM5, 6
Klick, M.: PS1-WeA11, **31**
Knappe, D.: SE+PS-TuA4, 21
Knoops, H.C.M.: EL+TF+AS+EM+SS+PS+EN+NM-MoM6, **2**
Ko, A.: PS-ThP34, 47
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Koay, C.: PS2-TuM9, 14
Kobayashi, M.: PS2-TuM6, 14
Koirala, P.: EL+TF+AS+EM+SS+PS+EN+NM-MoM4, **1**
Komachi, J.: PS2-ThM4, 37
Kometani, R.: PS2-ThM5, 37
Kondo, H.: PS1-TuM5, 12; PS2-MoA7, 11; PS2-ThM5, 37; PS2-WeA3, 32; PS-ThP14, 43
Kondo, Y.: PS2-MoA7, **11**; PS-ThP14, 43
Koshy, R.: PS-ThP1, 41; PS-WeM1, 28; PS-WeM4, 28
Koskey, S.: PS-WeM5, 29
Koster, N.B.: PS-ThA9, **40**; PS-ThP15, 43
Kotsugi, M.: GR+EM+NS+PS+SS+TF-MoM10, 4
Kroll, U.: PS-ThA3, 39
Krstev, I.: PS1-WeA10, 31
Kuang, Z.: GR+AS+BI+PS+SS-WeM6, 25
Kuboi, N.: PS2-ThM4, **37**
Kubota, T.: PS2-ThM11, 38; PS2-ThM9, 37; PS-MoM6, 6
Kulsreshath, M.: PS+EM-MoM3, 4
Kumar, A.: PS+EM-MoM8, **5**
Kumar, K.: PS2-TuM1, 13; PS-MoM5, 6; PS-ThP1, 41; PS-WeM4, 28
Kushner, M.J.: PS2-TuA11, **20**
Kwon, G.: PS+BI-MoA3, 8
Kwon, T.: PS2-TuM6, 14
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Labelle, C.: PS-ThP1, 41; PS-WeM1, **28**
Labonte, A.P.: PS-WeM1, 28; PS-WeM11, **29**
Ladroue, J.: PS1-ThM3, **35**
Lane, B.G.: PS1-TuM11, **13**; PS1-WeA12, 31
Laroussi, M.: SE+PS-TuA1, **21**
Lazzaroni, R.: PS+TC-WeM11, 27
Le Brizoual, L.: PS2-WeA10, **33**
Le, M.: PS-ThP10, 42
Lee, B.O.: PS-ThP23, 44
Lee, C.: PS2-TuM10, 15
Lee, G.: PS+BI-MoA3, 8
Lee, H.S.: PS-ThP29, **46**
Lee, J.: PS-WeM6, **29**
Lee, K.W.: PS-ThP23, 44
Lee, W.Y.: PS-ThP38, 47
Lee, Y.S.: PS-ThP23, 44
Lefaucheux, P.: PS+EM-MoM3, 4; PS1-ThM2, 35; PS1-ThM3, 35
Leick, N.: EL+TF+AS+EM+SS+PS+EN+NM-MoM6, 2
Lenox, C.: PS-MoM8, 7
Leou, K.-C.: PS-ThP45, 48
Leroy, P.: PS-ThP32, **46**
Levasseur, O.: PS+BI-MoA10, 9; PS+BI-MoA11, **9**; PS+TC-WeM1, 26

Lewin, E.: SE+PS-TuM5, 16
Li, A.-P.: GR+EM+NS+PS+SS+TF-MoM2, 3
Li, W.Y.: PS-ThA10, **40**
Liang, Y.: PS1-WeA3, 30
Liao, Y.C.: PS+EM-MoM4, 5
Lie, F.: PS2-TuM9, 14
Lien, S.-E.: PS-ThP45, 48
Ligot, S.: PS1-TuA8, **17**
Lii, T.: PS-MoM8, 7
Lim, W.S.: PS-ThP23, 44
Lin, P.A.: PS+EM-MoM8, 5
Lin, Q.: PS2-TuM6, 14
Lindsay, A.: SE+PS-TuA3, 21; SE+PS-TuA4, **21**
Ling, Z.: PS-ThA10, 40
Liu, C.: PS1-ThM12, 36
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Makabe, T.: PS+EM-MoM10, 5
Malinowski, A.: PS1-TuM5, 12; PS2-WeA3, **32**
Mankelevich, Y.: PS1-ThM2, 35
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Marot, L.: PS2-WeA1, 32
Marsillac, S.: EL+TF+AS+EM+SS+PS+EN+NM-MoM1, 1; EL+TF+AS+EM+SS+PS+EN+NM-MoM4, 1
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Milosavljevic, V.: PS1-TuM3, 12; PS1-WeA1, 30
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Miyashita, H.: GR+EM+NS+PS+SS+TF-MoM10, 4
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Moon, J.S.: GR+EM+NS+PS+SS+TF-MoM1, 2
Moon, S.Y.: PS2-WeA11, 33
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Morris, B.G.: PS2-TuM6, 14; PS2-TuM9, 14; PS-ThP1, 41; PS-WeM1, 28; PS-WeM11, 29
Mowll, T.: GR+EM+NS+PS+SS+TF-MoM2, 3
Mucha, J.A.: PS1-TuA10, 18
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Murphy, N.R.: SE+PS-TuM9, **16**
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Muthinti, G.R.: EL+TF+AS+EM+SS+PS+EN+NM-MoM9, 2
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Ranjan, A.: PS2-TuM1, **13**; PS-MoM5, 6
Ranjan, V.: EL+TF+AS+EM+SS+PS+EN+NM-MoM1, 1
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Robson, M.: PS-MoM1, 6
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Ross, N.: PS-WeM5, 29
Rosslee, C.: PS2-TuM2, 14
Rowe, J.E.: GR+AS+BI+PS+SS-WeM10, 26
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Sankaran, R.M.: PS+EM-MoM11, **6**; PS+EM-MoM8, 5
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Schuengel, E.: EN+PS-WeM12, 24; EN+PS-WeM9, **24**
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Schwaederle, L.: PS+EM-MoM3, 4
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Seong, D.J.: PS-ThP4, 41
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Shafiq, N.: GR+AS+BI+PS+SS-WeM2, 25
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Soda, E.: PS-ThP1, 41; PS-WeM4, 28
Song, I.: GR+EM+NS+PS+SS+TF-MoM4, 3
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Sozias, S.: PS+EM-MoM3, 4
Spooner, T.: PS2-TuM9, 14
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Sridhar, S.: PS-MoM8, 7
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Tan, X.: EL+TF+AS+EM+SS+PS+EN+NM-MoM4, 1
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Turchanin, A.: GR+AS+BI+PS+SS-WeM11, **26**
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Wang, Y.: PS-ThP10, 42
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Zhang, Q.: PS-ThP1, 41
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