Monday Morning, November 10, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+PS+SS+TF-MoM

2D Materials Growth and Processing
Moderator: Thomas Greber, University of Zurich

8:20am 2D+EM+NS+PS+SS+TF-MoM1 Exploring the Flatlands: Synthesis, Characterization and Engineering of Two-Dimensional Materials, *Jun Lou*, Rice University **INVITED**
In this talk, we report the controlled vapor phase synthesis of MoS_2 atomic layers and elucidate a fundamental mechanism for the nucleation, growth, and grain boundary formation in its crystalline monolayers. The atomic structure and morphology of the grains and their boundaries in the polycrystalline molybdenum disulfide atomic layers are examined and first-principles calculations are applied to investigate their energy landscape. The electrical properties of the atomic layers are examined and the role of grain boundaries is evaluated. More importantly, if precise two-dimensional domains of graphene, h-BN and MoS_2 atomic layers can be seamlessly stitched together, in-plane heterostructures with interesting electronic applications could potentially be created. Here, we show that planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically-patterned h-BN atomic layers. Our approach can create periodic arrangements of domains with size that ranging from tens of nanometers to millimeters. The resulting graphene/h-BN atomic layers can be peeled off from their growth substrate and transferred to various platforms including flexible substrate. Finally, we demonstrate how self-assembled monolayers with a variety of end termination chemistries can be utilized to tailor the physical properties of single-crystalline MoS_2 atomic-layers. Our data suggests that combined interface-related effects of charge transfer, built-in molecular polarities, varied densities of defects, and remote interfacial phonons strongly modify the electrical and optical properties of MoS_2, illustrating an engineering approach for local and universal property modulations in two-dimensional atomic-layers.

9:00am 2D+EM+NS+PS+SS+TF-MoM3 Influence of Substrate Orientation on the Growth of Graphene on Cu Single Crystals, *Tyler Mowll*, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *P. Tyagi, E.W. Ong, C.A. Ventrice, Jr.*, University at Albany-SUNY
A systematic study of graphene growth on on-axis Cu(100) and Cu(111) single crystals oriented within 0.1° from the surface normal and a vicinal Cu(111) crystal oriented 5° off-axis has been performed. Initial attempts to grow graphene by heating each crystal to 900°C in UHV, followed by backfilling the chamber with C_2H_4 at pressures up to $5x10^{-3}$ Torr did not result in graphene formation on either the on-axis Cu(100) or on-axis Cu(111) surfaces. For the vicinal Cu(111) surface, epitaxial graphene was formed under the same growth conditions. By backfilling the chamber with C_2H_4 before heating to the growth temperature, epitaxial graphene was formed on both the on-axis Cu(100) and off-axis Cu(111) surfaces, but not the on-axis Cu(111) surface. By using an argon overpressure, epitaxial overlayers could be achieved on all three Cu substrates. These results indicate that the most catalytically active sites for the dissociation of ethylene are the step edges, followed by the Cu(100) terraces sites and the Cu(111) terrace sites. The need for an argon overpressure to form graphene the on-axis Cu(111) surface indicates that the Cu sublimation rate is higher than the graphene growth rate for this surface. This research was supported in part by the NSF (DMR-1006411).

9:20am 2D+EM+NS+PS+SS+TF-MoM4 Synthesis of Large Scale MoS_2-Graphene Heterostructures, *Kathleen McCreary, A.T. Hanbicki, J. Robinson, B.T. Jonker*, Naval Research Laboratory
A rapidly progressing field involves the stacking of multiple two-dimensional materials to form heterostructures. These heterosctructures have exhibited unique and interesting properties. For the most part, heterostructure devices are produced via mechanical exfoliation requiring the careful aligning and stacking of the individual 2D layered components. This tedious and time consuming process typically limits lateral dimensions to micron-scale devices. Chemical vapor deposition (CVD) has proven to be a useful tool in the production of graphene and has very recently been investigated as a means for the growth of other 2D materials such as MoS_2, $MoSe_2$, WS_2, WSe_2 and hexagonal boron nitride. Using a two-step CVD process we are able to synthesize MoS_2 on CVD grown graphene. AFM, Raman spectroscopy, and Photoluminescence spectroscopy of the MoS_2-graphene heterostructure show a uniform and continuous film on the cm scale.

9:40am 2D+EM+NS+PS+SS+TF-MoM5 Growth of 2D MoS_2 Films by Magnetron Sputtering, *Andrey Voevodin*, Air Force Research Laboratory, *C. Muratore*, University of Dayton, *J.J. Hu*, Air Force Research Laboratory/UDRI, *B. Wang, M.A. Haque*, Pennsylvania State University, *J.E. Bultman, M.L. Jesperson*, Air Force Research Laboratory/UDRI, *P.J. Shamberger*, Texas A&M University, *R. Stevenson*, Air Force Research Laboratory, *A. Waite*, Air Force Research Laboratory/UTC, *M.E. McConney, R. Smith*, Air Force Research Laboratory
Growth of two dimensional (2D) MoS2 and similar materials over large areas is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. Typical preparation approaches with chemical or mechanical exfoliation lack scalability and uniformity over appreciable areas (>1 mm) and chemical vapor deposition processes require high substrate temperatures. We developed few-layer MoS_2 growth under non-equilibrium magnetron sputtering conditions selected to minimize the MoS_2 nucleation density and maximize 2D growth of individual crystals [1]. In this process, the thermodynamically driven tendency to form islands is accomplished by maximizing atomic mobility through the control of incident flux kinetic energies, densities, and arriving angle to the substrate while avoiding defect formation (i.e., vacancy creation by sputtering of S atoms). Amorphous SiO_2, crystalline (0001) oriented Al_2O_3, and (002) oriented graphite substrates were used to grow few monolayer thick MoS_2 films. Continuous 2D MoS_2 films were produced over 4 cm^2 areas. They were composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements with contact separation on the order of centimeters. Their characteristics were similar to few-layer MoS_2 films produced by exfoliation with a direct band gap in thin samples of approximately 1.9 eV from photoluminescense spectra. The electron mobility measured for as-grown MoS_2 films was very strongly dependent on film thickness and substrate choice.

[1] "Continuous ultra-thin MoS2 films grown by low-temperature physical vapor deposition", C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jesperson, P.J. Shamberger, A.A. Voevodin, Applied Physics Letters (2014) in press.

10:00am 2D+EM+NS+PS+SS+TF-MoM6 Formation of Graphene on the C-face of SiC{0001}: Experiment and Theory, *Jun Li, G. He, M. Widom, R.M. Feenstra*, Carnegie Mellon University
There are two {0001} surfaces of SiC, the (0001) surface known as the "Si-face", and the (000-1) surface or "C-face". The formation of graphene (by heating the SiC to 1100 – 1600 ° C in various gaseous environments) has been studied for both surfaces, although it is much better understood on the Si-face. In that case, an intermediate C-rich layer, or "buffer layer" forms between the graphene and the SiC crystal. This buffer layer has 6√3x6√3-R30° symmetry; its structure is well established,[1] and it acts as a template for the formation of subsequent graphene layers. In contrast, graphene formation on the C-face is much less well understood. More than one interface structure between the graphene and the SiC has been observed,[2,3] and, with one notable exception,[4] the quality of the graphene formed on the C-face is generally lower than that for the Si-face.

In this work we provide new experimental and theoretical results that allow us to understand graphene formation on the C-face of SiC. Experimentally, by heating the SiC in a disilane environment, we map out the phase diagram of different surface and interface structures that form on the SiC as a function of disilane pressure and sample temperature. New surface structures that develop just prior to the graphene formation are observed. With additional heating, graphene forms on the surface, but some remnant of the surface structure prior to the graphene formation is believed to persist at the graphene/SiC interface. From first-principles theory, we find that the hydrogen in the disilane environment plays a critical role in the surface/interface structures that form. Experimentally, for disilane pressures below $5x10^{-5}$ Torr, we find a 2x2 surface structure forming prior to graphene formation. From theory we identify this structure as consisting of a silicon adatom together with a carbon restatom on the surface, with H-termination of those atoms being possible but not necessary. At higher disilane pressures we observe a 4x4 structure, and we identify that as consisting of a lower density of Si adatoms than the 2x2, now with at least some of the adatoms and restatoms being H-terminated. With graphene formation, this structure converts to the observed √43x√43-R± 7.6° interface structure. At higher disilane pressures we theoretically predict the formation of a surface consisting simply of H-terminated carbon restatoms. Experiments are underway to observe that surface, along with subsequent graphene formation on the surface.

(1) Y. Qi et al., PRL **105**, 085502 (2010).

(2) F. Hiebel et al., PRB **78**, 153412 (2008).

(3) N. Srivastava et al., PRB **85,** 041404 (2012).

(4) W. A. de Heer et al., PNAS **108**, 16900 (2011).

10:40am 2D+EM+NS+PS+SS+TF-MoM8 Graphene on Hexagonal Boron Nitride Heterostacks Grown by UHV-CVD on Metal Surfaces, *Juerg Osterwalder, S. Roth, A. Hemmi,* University of Zurich, Switzerland, *F. Matsui,* Nara Institute of Science and Technology, Japan, *T. Greber,* University of Zurich, Switzerland   **INVITED**
Chemical vapor deposition (CVD) performed under ultra-high vacuum conditions on single-crystal metal surfaces enables the growth of large-area and high-quality graphene and hexagonal boron nitride (h-BN) single layers. We explore the CVD parameter space of precursor pressure and temperature in order to go beyond the self-saturating single-layer growth, or to grow heterostacks of the two materials. Formed layers are characterized structurally by LEED, STM and x-ray photoelectron diffraction. On Cu(111) a graphene layer could be grown on a pre-deposited single layer of h-BN when using 3-pentanone as a precursor at a pressure of 2.2 mbar and a substrate temperature of 1100 K [1]. On Rh(111) the same procedure leads to incorporation of carbon into the metal surface layers, while a graphene layer is formed only upon a second high-pressure dose [2]. In both cases the heterostructures show clearly the stacking sequence and structural and ARPES signatures of graphene on h-BN but are far from defect-free.

[1] S. Roth et al., Nano Lett. 13, 2668 (2013).

[2] S. Roth, PhD Thesis, Department of Physics, University of Zurich (2013).

11:20am 2D+EM+NS+PS+SS+TF-MoM10 Kinetics of Monolayer Graphene Growth by Carbon Segregation on Pd(111), *Abbas Ebnonnasir, H.S. Mok, Y. Murata,* University of California at Los Angeles, *S. Nie, K.F. McCarty,* Sandia National Laboratories, *C.V. Ciobanu,* Colorado School of Mines, *S. Kodambaka*, University of California at Los Angeles
In this research, using in situ low-energy electron microscopy and density functional theory calculations, we elucidate the growth kinetics of monolayer graphene on single-crystalline Pd(111). In our experiments, carbon saturated Pd(111) samples were cooled down from 900 ºC to segregate carbon on the surface in the form of graphene. Upon cooling the substrate, graphene nucleation begins on bare Pd surface and continues to occur during graphene growth. Measurements of graphene growth rates and Pd surface work functions along with DFT calculations establish that this continued nucleation is due to increasing C adatom concentration on the Pd surface with time. We attribute this anomalous phenomenon to a large barrier for attachment of C adatoms to graphene coupled with a strong binding of the non-graphitic C to the Pd surface.

Plasma Science and Technology
Room: 308 - Session PS-MoM

Current Challenges of Plasma Etching Technologies
Moderator: Saravanapriyan Sriraman, Lam Research Corp

8:20am PS-MoM1 Dielectric Etch Challenges and Evolutions, *Masanobu Honda*, Tokyo Electron Miyagi Limited, Japan   **INVITED**
For 7nm and beyond VLSI nano fabrication, fine process control in the order of nm or less is required, current incremental techniques may not address the challenges for future nano fabrication. In the High Aspect ratio processing such as 3DNAND and DRAM capacitor, miniaturization of the feature dimensions adds challenges to ion-radical transportation to the bottom of the feature, further aggravating etch yield and etch linearity. Further, in Logic MOL SAC, trade-off between the etch linearity and substrate recesses reduction are increasingly being focused. On the other hand, for BEOL interconnects, achievement of within-wafer uniformity of nm or less, and defect reduction at fine-node are added challenges. We have continued to challenge a variety of these dielectric etch issues, in order to provide technical solutions to enable future devices.

With further lithography related challenges and delays, complexity in patterning increases etch related challenges, continuous processing of the multilayer film with high accuracy corresponding to the multi-pattern is required. ARDE, reducing line roughness (LER/LWR), Trim, Hole Shrink and countermeasures in accordance with the thinning of the EUV resist are important challenges that etch has to overcome. We have effectively overcome these problems using unique resist treatment technologies based on high-speed electron beam and a sidewall protection film using DC super-imposed RF plasma system [1,2]. However, we still encounter trade-off

when solving these challenges, it is necessary to overcome the trade-off by introducing a new concept to enable further miniaturization.

As noted above, there are many challenges and potential tradeoffs to arrive at an optimal solution; we need a breakthrough to overcome these challenges. We have continued to explore and innovate solutions, as a result we are honing on a possible solution integrating etch and ALD techniques. Establishing this Etch-ALD concept and developing a robust flow will be a major breakthrough in overcoming patterning and other critical level issues related to nano-feature processing dielectrics and to sustain the Moore's Law.

Reference

[1] M. Honda et al., AVS 60th Int. Symp. & Exhibit. (2013)

[2] M. Honda et al., Proc. of SPIE 8328-09 (2012)

9:00am PS-MoM3 Improving Selectivity for 10nm BEOL Etch Using C5HF7 Gas, *Robert Bruce*, IBM T.J. Watson Research Center, *T. Suzuki, M. Nakamura,* ZEON Chemicals L.P., *A. Itou, G. Matsuura,* Zeon Corporation, *S.U. Engelmann, N.P. Marchack, E.M. Sikorski,* IBM T.J. Watson Research Center, *J. Lee,* IBM Albany Nanotech Center, *E.A. Joseph*, IBM T.J. Watson Research Center
As the industry moves to the 10nm technology node and beyond, new plasma etch challenges arise in the fabrication of back-end-of-line (BEOL) interconnects that need to be overcome. New materials and ever smaller critical dimensions require superior performance in etch, especially in minimizing line-edge roughness and low-k dielectric damage and improving hard mask selectivity. During dual damascene trench etch, low-k plasma damage leads to an increase in dielectric constant and pattern collapse. Also, during the self-aligned via (SAV) etch, vias short between one another due to poor metal hard mask selectivity and merging from via to via. Incorporating C5HF7 gas in these etch processes has shown significant improvements overall, because of its selective deposition properties. However, the C5HF7-based etch process needs to be tuned for the specific application, such as superior TiN selectivity for SAV or SiN selectivity for contact etch. In this talk, the optimized C5HF7-based processes for trench, SAV and contact are reviewed and compared. Furthermore, fundamental learning is accomplished using optical emission spectroscopy and x-ray photoelectron spectroscopy to understand the differences in mechanism between the various process regimes.

9:20am PS-MoM4 Effect of 147nm Photons on Porous Organo-Silicon Glass Materials and Damage Improvement by Optimized Cu/Low-k Integration Approaches, *L. Zhang,* IMEC, KU Leuven, Belgium, *Jean-Francois de Marneffe,* IMEC, Belgium, *M. Lukaszewicz,* Wroclaw University of Technology, Poland, *S. Barry-Porter, F. Vajda,* Trinity College Dublin, Ireland, *Y. Sun,* IMEC, Belgium, *M.H. Heyne,* IMEC, KU Leuven, Belgium, *M. Baklanov,* IMEC, Belgium
Porous organo-Silicon glass thin films, with porosities ranging from 8 to 48% and k-values from 2.7 to 1.9 were exposed to 147nm photons and ions emitted in a CCP discharge of Xe. The material changes have been measured by means of various surface and bulk analytical techniques. For high-porosity/low k-value, a strong Si-CH$_3$ depletion is observed, concomitant with moisture and increase of silanol group density. Surface densification occurs, as well as reduction of porosity. TOF-SIMS elemental profile indicate however that C and O profiles stay rather constant through the film thickness, only slightly changing in absolute value. Change of material properties are reflected in a rapid increase of the bulk dielectric constant. It is observed that 147nm VUV photons dissociate Si-C bonds, releasing -CH$_3$ and other H-based radicals in the porous matrix, reacting with dangling Si* and forming Si-H. It is shown that Si-H bonds are also dissociated by VUV but their loss is compensated until -CH$_3$ are completely dissociated. In absence of reactant to form volatile compound with, a major part of those radicals form complex polymers that condensate into the pores, while, upon ambient exposure, moisture react with remaining Si-dangling bonds forming highly polarizable silanol groups. The impact of VUV exposure on low-k dielectrics with varying porosities indicate a direct correlation between absolute Si-CH$_3$ loss and VUV dose, independent of inital methyl bond density. Change in dielectric properties (k-value) follows the same trend, showing, at fixed VUV dose, a dielectric shift $\Delta k = 1.0$ independent of the pristine k-value.

The observed trend suggest that, besides reactive radical diffusion, photons emitted during plasma processing do severely impede dielectric properties, and therefore need to be tackled appropriately during patterning and integration.

In order to reduce the impact of VUV, hardmasks with high photon absorption and the effect of polymer filling by the P4 or 'pore stuffing' approach were evaluated. Several mask materials were deposited on top of blanket OSG 2.0 low-k films and exposed to 147nm photons. Various polymers with different UV absorption properties were stuffed into porous

OSG 2.0 low-k films and then exposed to 147nm photons. For both cases, low-k damage was evaluated and showed reduced VUV damage.

9:40am PS-MoM5 Non-PFC Plasma Chemistries for Patterning Low-k Dielectric Materials, *Jack Kun-Chieh Chen, N. Altieri, M. Paine, T. Kim, J.P. Chang*, UCLA

Low-k materials, such as fluorine-doped and carbon-doped silicon dioxide, exhibit reduced dielectric constants necessary to curtail parasitic capacitance and avoid crosstalk in devices, keeping pace with the trend of increasing device densities. SF_6 and perfluorocarbons (PFC) gases, which are primarily used in plasma etch of interlayer dielectric materials, generally have high global warming potentials (GWP), making their increased usage undesirable. This work focuses on evaluating etch chemistries from a thermodynamic standpoint for back end of line (BEOL) applications in patterning of proposed low-k carbon-doped silica compounds with varying carbon content. Group and bond additivity methods were used to estimate the Gibbs free energies of formation for these carbon-doped compounds. PFC and non-PFC etchants with H_2/NH_3 were assessed through the use of volatility diagrams comparing partial pressures of volatile etch products as a function of etchant partial pressure at 300K. Minimization of Gibbs free energy was employed to calculate the equilibrium distribution of species in the etch system across a range of temperatures. NF_3 and CF_3I were identified as potentially viable for etching carbon-doped silica. NF_3, a non-PFC gas with an atmospheric presence of 1ppt, GWP of 16,800, and much greater abatement efficacy, is the most effective etchant in pure form, producing volatile etch product pressures between six and eight times that produced by CF_4. CF_3I, despite being an iodofluorocarbon gas, exhibited a GWP of unity and displays reduced damage to doped carbon, making it preferable in etching carbon-doped silica. Pure CF_3I shows reduced product pressure with increasing carbon content; however, addition of H_2 and NH_3 improves its performance for the three most highly doped silica compounds. Given the higher cost associated with using NF_3 and CF_3I, the introduction of an additive (H_2 or NH_3) was assessed. Addition of H_2 and NH_3 generally showed an increase in partial pressures predicted by the volatility diagrams, with H_2 producing a much more significant increase than the pure etchant or the addition of NH_3. Preliminary experimental results comparing etch rates for moderately to highly carbon-doped silica samples with 20 sccm CF_4 and hydrogen addition generally agree with theorized predictions. Varying the feed composition between 0%, 20%, and 50% H_2, etch rates of 38.2, 44.8 and 48.86 nm/min were recorded for lightly doped silica, and 49.2, 73.0 and 128.2 nm/min were recorded for heavily carbon-doped silica.

10:00am PS-MoM6 Optimization of the Optical Transmission of Submicron Silicon-on-Insulator Rib Waveguides, *Marc Fouchier, E. Pargon*, CNRS/UJF/CEA-LTM, France, *B. Ben Bakir, P. Brianceau, J. Harduin, S. Barnola, P. Grosse*, CEA-LETI, France

Optical interconnects have largely replaced copper for long distance data transmission and are gaining interest on shorter distances. At the intra-chip level, silicon waveguides are foreseen to relieve copper wire bottlenecks in the BEOL layers. The strong light confinement allowed by the large refractive index difference between Si and SiO_2 permits the building of submicron silicon on insulator (SOI) waveguides with small bending radii and thus of compact photonic circuits. However, the strong light confinement also results in large propagation losses due to the scattering of the guided light on the rough etched sidewalls of the silicon core. Modeling shows that the transmission loss mostly depends on the line edge roughness (LER) of the guide and on its correlation length.

In the present work, we apply our silicon processing and sidewall roughness metrology know-how developed for transistor gates to optimize the fabrication process of submicron rib waveguides on 200 mm SOI wafer in order to reduce their optical loss. First SiO_2 and photoresist etch masks are evaluated. In both cases, the eventual benefit of an HBr plasma cure treatment, originally developed for FEOL processing, on the photoresist is also assessed. Second, we investigate the impact of several silicon smoothing strategies on the patterned waveguides: thermal oxidation and hydrogen annealing. Oxidations are performed in pure O_2 at 1000°C, above the SiO_2 viscous transition. The following thicknesses are tested: 5, 10, 30 and 3×10 nm. Oxidizing in three steps compared to a single longer step is believed to increase LER reduction because smoothing is faster in the initial reaction limited regime than in the subsequent diffusion limited regime. Hydrogen annealing is performed in pure H_2 for 2 min at several temperatures between 850 and 1000°C. After each process step the LER is measured by CD-SEM. In order to obtain LER values freed from instrumental noise and their correlation length, CD-SEM data are treated by spectral analysis . At the end of the process, the sidewall roughness of the rib waveguides is also characterized by AFM on a tilted sample. In addition, their profile is measured by cross-sectional SEM and their transmission loss on an optical test bench.

Measurements show that a resist mask is better than the SiO_2 mask for minimizing optical attenuation at the price of a degraded profile while the

photoresist cure treatment does not have much influence. Further experiments are ongoing to evaluate the impact of the silicon smoothing processes (hydrogen annealing or thermal oxidation) on the roughness and to correlate it with optical loss measurements.

10:40am PS-MoM8 Using Post Etch Treatment (PET) to Resolve Poly Residue Defect Issue of Dummy Poly Removal (DPR) in hi-K Metal Gate Processing, *Chih-Chien Wang, F.Y. Chang, C. Li-Chiang, S.-Y. Lu*, United Microelectronics Co., Taiwan, Republic of China, *P.-W. Huang, Y.-C. Kao, S.-Y. Cheng, T.-T. Su*, Lam Research Corporation

Dummy Poly Removal (DPR) is one of the critical processes of hi-K metal gate formation of gate last integration scheme of semiconductor wafer fabrication. A typical DPR process flow includes plasma etching a wafer to open hardmask and to remove dummy poly, then wet etch the wafer with Tetra-Methyl Ammonium Hydroxide (TMAH) to remove any residue that is remained inside the dummy gate trench.

Amorphous silicon is commonly used as the dummy poly materials. A plasma composed of Cl2, HBr, NF3, or combination of above is used to dry etch the dummy poly; however, poly residue defect is observed after DPR process flow. Experimental data indicates that after plasma etch, a Si-O layer is formed on the surface of amorphous silicon which suppress the dummy poly removal capability of the subsequent wet etch. Therefore, dummy poly material is left behind and forms the poly residue defects.

If extended plasma is used to remove the poly residue, the barrier layer (TiN) will be etched and thus damage the hi-K.

To resolve the poly residue defect issue, a post etch treatment (PET) is added after dummy poly is etched by plasma. The purpose of PET is three-folded: it converts the Si-O layer to a layer of which wet etch rate is significantly improved; PET activates the residual F, Cl or Br inside the gate trench and enhance the poly removal; PET has high selectivity to the barrier layer (TiN) and thus TiN film is preserved. The result is no poly residue defects and no hi-K damage.

11:00am PS-MoM9 Sidewall Roughness Characterization of an Advanced Spacer Patterning Process, *Emmanuel Dupuy, M. Fouchier, E. Pargon*, CNRS-LTM, France, *J. Pradelles*, CEA-Léti, France, *H. Grampeix*, CEA-LETI, France, *P. Pimenta-Barros, S. Barnola*, CEA, LETI, France, *O. Joubert*, LTM - CEA/LETI, France

Line width roughness (LWR) or line edge roughness (LER) is considered today by the microelectronic industry as a critical factor limiting CMOS transistors downscaling. According to the international technology roadmap for semiconductors, LWR and LER values must be controlled below 2 nm for the next sub-20 nm nodes, which remain a technological challenge for all nanopatterning options and metrology tools. Understanding and minimizing LER at this nanometer scale thus requires an accurate and insightful characterization of the sidewall roughness.

Among advanced nanopatterning solutions, spacer patterning has emerged as a reliable and competitive technique to fabricate fine patterns down to 10 nm. This technique consists in depositing a spacer material on each side of a core (mandrel) defined by lithography and then removing the core to halve the pitch. One critical aspect of this approach is the control of the LER since the spacer patterns are asymmetric from their formation. The right and left sides of the spacer are not obtained by the same technological step and could lead to different LER values on the left and right sidewalls. This behaviour could be problematic if this asymmetry is transferred to the final pattern.

In this work, we propose to characterize and evaluate finely the LWR/LER evolution after each technological step involved in a resist-core spacer patterning process targeting a half-pitch of 20 nm and 10 nm. In this particular case, spacers are directly deposited on the side of the resist. Advantages are less processing steps, a simplified stack and a reduced production cost. A method based on a power spectral density (PSD) analysis is used take into account the noise level of CDSEM images in the LWR/LER estimation of these fine patterns. A full description of the sidewall roughness including its spatial frequency distribution is obtained at each step with an estimation of noise-free parameters such as roughness amplitude (3Ơ), correlation length (ξ), and roughness exponent (α)." For the 20 nm node, LWR and LER values are drastically reduced to 2.5nm and 2.2nm respectively. The correlation length is found to range from 8 to 22 nm and the roughness exponent from 0.4 to 0.9 for the final silicon lines. Results for the 10 nm node will be discussed in view of evaluating and optimizing process performances.

11:20am PS-MoM10 Improving Pattern Fidelity for Selective Etch Processes, *Nathan Marchack, S.U. Engelmann, E.A. Joseph, R.L. Bruce, H. Miyazoe, E.M. Sikorski*, IBM T.J. Watson Research Center, *T. Suzuki, M. Nakamura*, ZEON Chemicals L.P., *A. Itou, H. Matsumoto*, Zeon Corporation

As critical dimensions and pitch sizes of integrated circuit technologies continue to decrease, the challenges associated with maintaining pattern transfer fidelity become especially difficult to surmount. LER/LWR, CD variation, iso/dense feature loading and deformation of the organic soft masks are commonly observed phenomena. Other issues include extensive plasma damage or mask retention for post-lithography solutions.[1]

Our team recently introduced a new etch gas which is able to etch nitride by selective deposition of a fluorocarbon layer[2], analogous to the well established oxide etch mechanism commonly used in manufacturing.[3] Selective deposition was achieved by redesigning the FC etch gas, where reaction with a nitride substrate layer reduces the FC film thickness compared to silicon or oxide substrates. Owing to the complex, distinct nature of the reaction pathways offered by this new plasma chemistry, optimizing the etch performance involves tuning plasma parameters that have not been traditionally investigated. We have evaluated the influence of substrate and showerhead temperatures, gas admixture chemistry and plasma pulsing on the performance of this etch gas for hard mark patterning applications.

By tuning the chemical admixture of the plasma, 50nm pitch patterning of an 80nm thick nitride hard mask layer using a 65nm carbon mask was achieved with greatly reduced LER/LWR (~2.3/2/7) and minimal iso/dense feature loading compared to a traditional CF_4/CHF_3 mixture (LER/LWR ~5/8). The use of plasma pulsing, as well as lowering the lid temperature, was found to increase the carbon mask retention while maintaining reduced LER/LWR. The effect of lid temperature was shown to be related to gas dissociation, which was observed through full spectrum OES spectra collected. The improved mask retention under these conditions allowed for LER/LWR to be reduced even further by reducing the aspect ratio of the structures.

1. S. Engelmann et al., Proc. SPIE 8328-9

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

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

Advanced Surface Engineering
Room: 302 - Session SE+EM+EN+PS+TF-MoM

New Developments in Atmospheric Pressure Plasma Deposition and Thin Films for Energy Applications
Moderator: Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:40am SE+EM+EN+PS+TF-MoM2 Real Time Characterization of Polymer Surface Modification by an Atmospheric Pressure Plasma Jet, *Andrew Knoll, P. Luan, E.A.J. Bartis, C. Hart*, University of Maryland, College Park, *Y. Raitses,* Princeton Plasma Physics Laboratory, *G.S. Oehrlein*, University of Maryland, College Park

Atmospheric pressure plasma jets (APPJ) have been shown to modify surfaces, leading to a variety of potential industrial and medical applications. APPJ treated surfaces are typically evaluated post treatment, but few studies exist showing surface changes in real time. In this study, we characterized both closely-coupled and remote APPJ treatments of a PMMA-based 193 nm photoresist polymer (PR193) using *in situ* ellipsometry to monitor film thickness and refractive index in real time. The kilohertz-driven, two-ring electrode APPJ was fed with low admixtures of O_2 and N_2 to Ar. Voltage and current waveforms were collected to electrically characterize the APPJ and measure power dissipation. In addition, high speed photography of the APPJ was conducted in order to characterize plasma interaction with various controlled environments and with PR193. Ellipsometry shows that PR193 etch rates depend on the feed gas chemistry and treatment time. Etch rates are reduced for Ar/O_2 compared with pure Ar and Ar/N_2. This reduction is correlated to a decrease in plasma density with O_2 addition. It is also shown that the etch rate changes over time initially during APPJ heating and reaches steady state as the temperature stabilizes. When the plasma is brought close enough to the sample, the discharge couples with the surface and arcing in the film occurs. This interaction greatly increases the etch rate and introduces major damage to the polymer, which can be observed by the naked eye. From electrical data and high speed photography we see that the pure Ar discharge exhibits filamentary behavior that is enhanced by O_2 addition and rendered more diffuse by N_2 addition. High speed photography shows that the coupling of

the plasma and the environment increases when the environment matches the feed gas chemistry, which causes the plume to extend farther than in open air. While the Ar plume is confined to a single plasma channel, N_2 admixture to Ar branches out into many smaller discharges, similar to a Lichtenberg figure. We also correlate damage seen on the polymer surface with observed arcing. The authors gratefully acknowledge financial support by US Department of Energy (DE-SC0001939).

9:00am SE+EM+EN+PS+TF-MoM3 Gas-Liquid Mixed Phase Plasma at Atmospheric Pressure, *Akira Ando, G. Tang, R. Ohno, A. Komuro, K. Takahashi*, Tohoku University, Japan **INVITED**

A gas-liquid mixed phase plasma discharge is investigated using nanosecond high-voltage pulse generator. Non-thermal atmospheric pressure plasmas have recently attracted significant attention due to their good energy efficiency in production of reactive species. Plasma in water can generate many reactive species, such as ozone, hydroxyl radicals and oxygen radicals. These products have strong oxidizing power and is applicable for many applications without any thermal stress.

We have utilized a nanosecond high-voltage pulse to produce a discharge within bubbles introduced into water, where semiconductor opening switching (SOS) diodes are used in the pulse generator.

The reactor for the gas-liquid hybrid plasma consists of two regions, gas and liquid regions, separated by a thin plate with a small holes (1mm in diameter). Several working gases are fed into the reactor from the gas region and bubbles are formed via the separator holes in the water. High-voltage pulse with 10-15kV are applied to a wire electrode situated in the gas phase. A grounded electrode is set into the water. When the high voltage pulse with the duration of 40ns is applied, a streamer-like discharge occurs within the bubbles and the streamer extends along the surface of gas-liquid interface.

The formation process of discharge bubbles were observed with a high-speed CCD images of the discharge. The area of discharge extension depends on the gas species and conductivity. Production rate of reactive species, ozone and hydroxyl radicals in a discharge reactor was also depends on the parameters. As the life time of hydroxyl radicals is very short, the amount is estimated from concentration of hydrogen peroxide produced in treated water, which is produced by the recombination process of hydroxyl radicals.

In order to evaluate the oxidation power in the gas-liquid mixed plasma, we applied it to water purification, such as decolorization, sterilization and decomposition of persistent organic pollutants (POPs). The sterilization effect in the water is estimated from the survival ratio of bacillus subtilis and it reaches more than 99.5% after 15min treatment. The survival ratio is large in air discharge and the value of pH in water as well as ultraviolet (UV) ray generated by plasma discharge affects the sterilization. SEM images shows the surface of the bacteria were damaged by the treatment.

9:40am SE+EM+EN+PS+TF-MoM5 Atmospheric Pressure High Power Impulse Plasma Source (AP-HiPIPS) for Plasma Enhanced Chemical Vapor Deposition of Thin Films, *Vasiliki Poenitzsch, R. Wei, M.A. Miller, K. Coulter*, Southwest Research Institute

Southwest Research Institute is currently developing a High Power Impulse Plasma Source (HiPIPS) that supplies a high flux of energetic reactants to a surface while maintaining a low processing temperature. HiPIPS is a new plasma enhanced chemical vapor deposition technology that combines variable pressure plasma jets with advanced pulsed power technology. Several complementary techniques, including mass spectroscopy, optical emission spectroscopy (OES) and electrical and thermal probes were employed, for measuring and calculating the plasma characteristics in a wide range of the HiPIPS process parameters and conditions. The preliminary HiPIPS experiments have revealed that high peak power (~40 kW) in the pulses can be achieved resulting in a high peak current (~200 A) and increased plasma density (i.e. n = Ar: 10^{20} cm^{-2}s^{-1}) while maintaining a low average power (35W) and a low substrate processing temperature (50-150 °C). A prototype atmospheric-pressure HiPIPS (AP-HiPIPS) was successfully developed and proof-of-concept AP-HiPIPS diamond-like carbon (DLC) film deposition was demonstrated. Beyond DLC films, HiPIPS plasmas could be applicable to deposition of many classes of films and many types of surface treatments. In contrast to conventional state-of-the-art non-thermal atmospheric pressure plasma jets, typically driven by RF or AC, the power densities and currents during pulse on-time are 2-3 orders of magnitude higher in HiPIPS. Since plasma is created through inelastic electron collision with precursor gas molecules, the increased power and current directly equates to significantly improved ionization and dissociation of precursor gases in HiPIPS. Thus, distinguishing features of HiPIPS as compared to RF or AC APPJs are increased ionization, enhanced molecular gas dissociation, and higher flux of reactive species while maintaining the same low deposition temperatures. In this presentation, an

overview of HiPIPS and AP-HiPIPS will be given with a specific focus on plasma characteristics and areas for further development.

10:00am SE+EM+EN+PS+TF-MoM6 Importance of Argon's Spectral Emission for Plasma Diagnostics at an Atmospherics Open Air Plasma Discharge, *Vladimir Milosavljevic, J. Lalor, P. Bourke, P.J. Cullen*, Dublin Institute of Technology, Ireland

In recent years, plasma on atmospheric pressure attracts a lot of attention due to their numerous applications in plasma biology, health care, and medicine, as well as surface and materials processing and nanotechnology. Among several atmospheric pressure plasma devices, a dielectric barrier discharge plasma jet (DBDPJ) is the most used, because of its simplicity and a fact that the generated plasma is in surrounding air and not in a confined space. The dynamics of DBDPJ in noble gases reveal that the plasma plumes propagate at a speed several orders of magnitude higher than the gas flow velocity. This is why it is generally accepted that the propagation of the plasma plumes is driven electrically rather than by the gas flow, which imposes in the first place the importance of the plasma diagnostics. Because of the frequent collisions between electrons and neutrals at high pressure, the electrical probe methods are generally less useful for plasmas produced at atmospheric pressure. Therefore, other diagnostic methods are needed and optical emission spectroscopy (OES) has been used as one of the alternative diagnostics because of its simplicity and non-intrusive nature.

Nitrogen dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. Nitrogen acts as a 'sensor gas' and OES diagnostics are applied in assumption that most nitrogen molecular emissions are excited during electron impact of ground state N2(X). When nitrogen is added/mixed with argon plasma discharges, the argon emission lines are significantly quenched and the resulting plasma spectral emission is changed. Measurements and analysis of neutral argon spectral emission lines give very important information about the plasma properties. In this work the absolute spectral emissions of the atomic and molecular lines associated with argon, oxygen, nitrogen and hydrogen are presented. Wavelength resolved optical emission profiles of argon's spectral lines shows that the change in electron energy distribution functions (EEDF) has taken place for a low gas flow rate only. After the gas flow rate goes above a certain limit, the EEDF remains constant. At the same time the density of argon metastable atoms are changed with the gas flow rate. Overall, analysis of the spectral intensities assist in the development of optimised plasma processing parameters for treatments such as surface activation or removal of contaminates.

10:40am SE+EM+EN+PS+TF-MoM8 Hot 'n Flaky: Thermal Properties of Layered Atomic Structures, *Christopher Muratore*, University of Dayton, *V. Varshney*, Air Force Research Laboratory/UTC, *J.J. Hu*, Air Force Research Laboratory/UDRI, *A.A. Voevodin*, Air Force Research Laboratory **INVITED**

Synthesis capability for uniform growth of 2D materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. We have demonstrated, for the first time, vapor phase growth techniques for precisely controlled synthesis of continuous, uniform molecular layers of all MoX_2 and WX_2 transition metal dichalcogenide (TMD) compounds on diverse substrates, including graphene, hexagonal boron nitride, highly oriented pyrolitic graphite (HOPG), SiO_2, and metal substrates over several square centimeters. Preliminary results show MoX_2 and WX_2 transition metal dichalcogenide materials grown in a novel ultra-high vacuum (UHV) physical vapor deposition (PVD) process demonstrate properties identical or even superior (e.g., electron mobilities >500 cm^2 V^{-1} s^{-1}) to exfoliated layers. Growth of bi-layer MoS_2 on few-layer graphene with a 30% lattice mismatch and TMD/TMD heterostructures are shown to demonstrate how natural accommodation of stresses at 2D van der Waals interfaces has the remarkable potential to transform the way materials selection is considered for synthetic heterostructures, as concerns regarding lattice constant matching can be abandoned with preference given to desired properties and performance. Investigations relating to application of these materials in thermoelectric device applications are presented. Thermal conductivity values of TMD thin films were compared to bulk crystals, revealing expected trends with mass, but a >10 fold reduction in thin film thermal conductivity. Phonon scattering lengths at domain boundaries based on computationally derived group velocities were consistent with the observed film microstructure, accounting for the reduction. We also explore thermal anisotropy in MoS_2 films. Measurement results are correlated with MD simulations of thermal transport for perfect and defective MoS_2 crystals, demonstrating the importance of thermal boundary scattering.

Thin Film
Room: 305 - Session TF+PS+SE-MoM

Advanced PVD Methods
Moderator: Subhadra Gupta, University of Alabama

9:00am TF+PS+SE-MoM3 Ternary and Quaternary Thin Layers Deposited by Magnetron Sputtering, *Marie-Paule Besland, J. Tranchant, E. Janod, C. Benoit, L. Cario, P.Y. Jouan, M. Carette, A. Lafond,* Institut des Matériaux Jean Rouxel – Université de Nantes, France, *R. Meunier, S. Fabert,* Institut des Matériaux Jean Rouxel – Université de Nantes and Crosslux, France, *P.Y. Thoulon, M. Ricci*, Crosslux Company, France

Developing new functionalities mainly depend on the use of new functional material. Nevertheless, prior to envision any development of functional materials towards devices, two major challenges have to be tackled. The former one is to obtain thin layers of active and functional materials. The second challenge is to recover the functional properties on thin layers. For several decades, magnetron sputtering is a widely used deposition technique in microelectronics. Moreover, magnetron sputtering enables to deposit well-crystallized film of insulating or conducting materials, at low temperatures, over large areas, while controlling the film composition and microstructure, even for complex and multi-component materials. Thus, on the basis of well established know-how in deposition process and multi-layered functional structures [1], the deposition of GaV_4S_8 material in the form of thin layers has been investigated by both non-reactive RF magnetron sputtering and reactive process in Ar/H_2S mixture [2]. While the functionality (Resistive switching =RS) was first evidenced on single crystals, our studies demonstrated that metal-insulator-metal (MIM) structures based on GaV_4S_8 thin layers, deposited by magnetron sputtering, exhibit as well a similar RS [3]. More recently, we focus on the historical chalcogenide absorber for solar cells: CIGSe. We developed a dedicated and home-designed vacuum chamber for CIGSe thin films deposition using "one step sputtering". In that study, CIGSe thin films were deposited on SLG/Mo substrates by RF magnetron sputtering and then ex-situ annealed under controlled atmosphere. Deposition and annealing parameters can modify both chemical composition and structural properties. In particular, different preferential crystalline orientation may be induced and can modify functional properties in a large extend. Finally, the performances of CIGSe solar cell completely realized by magnetron sputtering technique will be compared to published efficiency values in the 8.9- 10.5 % range [5].

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9:20am TF+PS+SE-MoM4 Molecular Dynamics Simulations of TiN/TiN(001) Growth, *Daniel Edström, D.G. Sangiovanni, V. Chirita, L. Hultman,* Linköping University, Sweden, *I.G. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign

The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward s understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with Ab Initio MD based on Density Functional Theory (DFT) [3], [4]. Half a monolayer of TiN is deposited on 100x100 atom TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 125 ns. The TiN substrate is maintained at a typical epitaxial growth temperature, 1200 K during deposition using Ti:N flux ratios of 1:1 and 1:4 with incident atom energies of 2 and 20 eV to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2

eV incidence energy, islands begin to form atop existing islands at coverages $\gtrsim$ 0.25 ML, leading to 2D multilayer growth. At 20 eV, the film growth mode shifts toward layer-by-layer growth. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

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9:40am TF+PS+SE-MoM5 Surface Chemistry of Pd and Ag Interaction with 3C-SiC Thin Films Deposited on Si(111) by Pulsed Laser Depositon, *Rachel Seibert, D. Velazquez, J. Terry*, Illinois Institute of Technology, *K.A. Terrani, C. Baldwin, F. Montgomery, K. Leonard, J. Hunn, P. Schuck, R. Stoller*, Oak Ridge National Laboratory, *S. Saddow*, University of South Florida

The surface interactions of nuclear fission products with the barrier SiC layer of Tri-Structural Isotropic (TRISO) coated fuel particles limit fuel cell performance. In particular, Pd and Ag reduce the structural integrity of SiC. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors, but currently is not well understood. This surface chemistry is examined both in spent TRISO fuel on SiC/Si(111) thin films and compared to theoretical calculations done by Schuck and Stoller at Oak Ridge National Laboratory [1]. Synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were conducted on the irradiated TRISO fuel pellet to characterize atomic interactions at the Pd K-edge (24350 eV). The thin films were grown epitaxially via pulsed laser deposition (PLD), as evidenced by reflection high energy electron diffraction (RHEED) patterns. Pd and Ag were deposited on separate SiC/Si(111) films in thickness increments from 0.5-5 monolayers. The chemical structure of the thin films is analyzed using X-ray photoelectron spectroscopy (XPS).

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10:00am TF+PS+SE-MoM6 High Thermal Stability Nanocrystalline Gold, Part I, *Ronald Goeke*, N. Argibay, J.E. Mogonye, K.M. Hattar, S.V. Prasad, Sandia National Laboratories

Gold coatings that are ideally suited for low electrical contact resistance (ECR) applications are mechanically soft and exhibit unacceptable amounts of adhesion and friction. To mitigate these problems gold for ECR applications is typically alloyed with Ni, Co or Fe which increases the film hardness and wear resistance. A key limitation of hard gold coatings is the propensity for the non-noble alloying metal species to diffuse to the surface and form non-conductive oxide films that can severely impact the electrical contact behavior. These traditional hard gold films, which are fabricated via electro-deposition, have been limited to electrochemical compatible materials. Using co-deposition of Au-ZnO by electron beam evaporation we have eliminated the electrochemical material limitations and synthesized a new class of hard gold thin films. The ceramic phase is used to strengthen the composite via grain refinement. The resulting nanocrystalline gold thin film can replace typical hard gold films and exhibits enhanced thermal stability as the refractory ceramic phase is kinetically limited and has no oxidative potential for migration to the surface. The synthesis, characterization, and thermal stability against grain sintering will be discussed.

10:40am TF+PS+SE-MoM8 High Thermal Stability Nanocrystalline Gold Thin Films, Part II, *Nicolas Argibay, J.E. Mogonye, R.S. Goeke, K.M. Hattar, M.T. Dugger, S.V. Prasad*, Sandia National Laboratories

In the second part we present the result of investigations of the bulk transport properties, thermal and mechanical stability, and mechanical properties of electron beam codeposited Au-ZnO as a function of composition and temperature (up to a homologous temperature of 0.5). A high throughput method for determining the average grain size in electrically conductive metal-ceramic thin films will be presented, founded on a correlation between grain boundary density and electrical resistivity (Mayadas-Shatzkes and Sondheimer-Fuchs models), and compared to microstructural characterization using backscatter and transmission electron diffraction, SEM, and XPS.

11:00am TF+PS+SE-MoM9 Growth and Phase Stability of Zirconium Diboride Thin Films, *David Stewart, D.J. Frankel, R.J. Lad*, University of Maine

Zirconium diboride (ZrB_2) has metallic-like electrical and thermal conductivities up to its melting point of 3246°C and is also thermal shock resistant, making it an excellent material for use in harsh, high temperature environments. Presently, much of the literature on boride materials concerns bulk, sintered materials, and less is known about ZrB_2 thin films. Here we demonstrate the growth of ZrB_2 thin films by e-beam co-evaporation of elemental Zr and B sources on sapphire, silicon, and silica substrates. Films were deposited over a range of Zr:B compositions and were characterized before and after annealing up to 1000°C in air or under vacuum (10-8 Torr). Scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) indicated that as-deposited films are homogeneous, with a smooth morphology and covalent bonding character. X-ray diffraction (XRD) revealed that films deposited at temperatures from ambient to 600°C are typically amorphous, and annealing in vacuum up to 1000°C can cause the formation of a ZrB_2 crystalline phase that coexists with an amorphous matrix, depending on the Zr:B ratio. Films annealed in air as low as 800°C become heavily oxidized and boron-depleted, leaving behind a monoclinic ZrO_2 polycrystalline film. XPS depth profiles suggest the formation of a boron oxide phase in air that evaporates from the surface at high temperatures, consistent with surface oxidation behavior reported for bulk ZrB_2 materials. Electrical conductivities of as-deposited films, measured with a 4-point probe, range from $0.3 – 8.3 \times 10^6$ S/m depending on the Zr:B ratio, and the films retain their conductive nature after vacuum annealing. The ZrB_2 crystalline phases exhibit a preferred (100) crystallographic texture, and valence band XPS measurements confirm the existence of hybridized B2p-Zr4d bonding states. Understanding the high temperature stability of ZrB_2 films is important for developing it as a potentially stable conducting film for electronic device applications in harsh environments.

11:20am TF+PS+SE-MoM10 Thickness Dependence of High Frequency Magnetic Properties for Thin Films of Iron-Gallium-Boron, *Colin Rementer, Y. Kim, J.P. Chang*, University of California at Los Angeles

Iron gallium boron, i.e. $(Fe_{80}Ga_{20})_xB_{1-x}$ or FeGaB, is a material of considerable interest for high frequency, multiferroic applications. Lou *et al.* discovered that the addition of boron to the magnetostrictive material Galfenol ($Fe_{80}Ga_{20}$ or FeGa) led to a decrease in coercivity (~1 Oe), decrease in ferromagnetic resonance (FMR) linewidth (~20 Oe) at X band, and an increase in piezomagnetic coefficient (~7 ppm/Oe). The physical properties were optimized in $(Fe_{80}Ga_{20})_{88}B_{12}$ with ~100 nm thickness (Lou, J. et al. 2007). The material has been incorporated into several multiferroic systems with great success (Lou, J. et al. 2009). It is a material of great interest for integration into various multiferroic antenna systems. To have a better understanding of the material, a more thorough study on the fundamental properties of the material at different thicknesses is needed, as well as how that thickness can affect the tunability of resonant frequency and magnetoelectric coupling in multiferroic heterostructures when incorporated with ferroelectric single crystals.

FeGaB was grown via co-sputtering of $Fe_{80}Ga_{20}$ and boron targets via DC magnetron and RF magnetron sputtering, respectively. The FeGa target was held at 60 W and the boron power was adjusted to tune the boron concentration, from 9 - 18%. FeGaB films were grown with thicknesses ranging from 30 nm – 500 nm, and a growth rate of 7 nm/min was achieved. The coercivity and saturation magnetization of the FeGaB films decreased (~10 Oe), and increased (1200 emu/cc), respectively, with decreasing thickness (30 nm). Ferromagnetic resonance (FMR) linewidth was measured at X band (9.6 GHz), and it was found that it narrowed to 140 Oe with decreasing thickness at 30 nm. Both $Fe_{75}Ga_{25}$ and $Fe_{60}Ga_{22}B_{18}$ were

shown to be magnetoelastic, having magnetostriction constants of around 30 ppm and 60 ppm, respectively. The magnetic properties of FeGaB are being optimized to the properties measure by Lou et al. to ensure the rigor of the thickness dependence study (Lou, J. et al. 2007). The effect of inducing stronger in-plane anisotropy in the FeGaB films was investigated via an *in situ* magnetic field applied during deposition, and post-deposited magnetic annealing is being explored as a function of thickness.

11:40am TF+PS+SE-MoM11 Optimizing Magnetic Confinement for High Productivity PVD System Linear Scanning Magnetron, *V. Kudriavtsev, Robert Norris, T. Bluck, I. Latchford*, Intevac, Inc.
High productivity vacuum PVD system cost of ownership is very sensitive to sputtering target utilization. In this paper we discuss magnetic array design methodology that is required to achieve excellent plasma confinement that can lead to most uniform target erosion both magnetic and nonmagnetic targets. Design trade-offs are more challenging when using highly magnetic target materials, such as Nickel. These materials have lower PTF (pass through flux) and also affect magnetic field in all directions. Stronger magnets allow the fields to penetrate magnetic target material and judicious design process allows minimizing negative effects of field shunting.

First we develop static magnetic simulations model; magnetic properties are assigned to magnets, magnetic materials and also properties to nonmagnetic elements. Resulting computations are presented in a form of magnetic field component and Bz component on the surface of the target or in the vicinity of that surface. The magnetic track is determined by searching for locations where perpendicular component of magnetic field Bz=0 and we review variations in Bx and By along this track. Magnetic field characteristics are studied at various distances from magnets, sizing the magnetic array configuration, magnet dimensions, and their polarity for a selected objective. Usually this objective is to provide certain field strength at certain distance away from magnets. One can increase the strength of N or S polarity in the array, creating balanced or unbalanced magnetron configuration, that affect maximum field strength, erosion profile and erosion in the middle of the target where the absolute value of magnetic field reaches a maximum. Magnetic field characteristics are extracted from the erosion track profile and theoretical erosion profile is calculated resulting from the current array design. These profiles allow estimation of the "static" target utilization and if necessary to create optimization cycle where magnetic characteristics of the design (parameters) are computationally changed to reach desired erosion profile. Once the final computer design is selected, engineers build the first prototype of magnetic array and evaluate its magnetic properties using a 2d magnetic scanner that provide B, Bx, By, Bz components of magnetic field in plane on a distance from magpack. The next step of the analysis utilizes experimentally extracted magnetic field (or previously computed theoretical magnetic field) to estimate resulting 2D erosion profile that is due to the magnet non-uniform and non-linear motion. Finally, using the ray tracing method we perform film uniformity analysis for a substrate of given size which is located on a defined distance away from the sputtering target. That analysis is transient and factors in substrate nonlinear motion. Resulting film uniformity is estimated as a superposition of multiple substrate positions as it moves under the target.

Thin Film
Room: 307 - Session TF+PS-MoM

Atmospheric, Roll-to-Roll and other Manufacturing Advances in ALD
Moderator: Paul Poodt, Holst Centre / TNO

8:20am TF+PS-MoM1 Barrier Properties of Plastic Films Coated with Al₂O₃ by Roll-to-Roll ALD, *Charles Dezelah*, Picosun USA, LLC, *T. Hirvikorpi, R. Laine, W.-M. Li,* Picosun Oy, Finland, *M. Vähä-Nissi, E. Salo,* VTT Technical Research Centre of Finland, *V. Kilpi, S. Lindfors,* Picosun Oy, Finland, *J. Vartiainen, E. Kenttä, J. Nikkola, A. Harlin,* VTT Technical Research Centre of Finland, *J. Kostamo,* Picosun Oy, Finland
INVITED
Atomic layer deposited (ALD) Al₂O₃ has proven to be effective in enhancing the moisture and gas barrier properties of various plastic films and coatings [1-3]. The key challenge in several applications is to find a flexible, reliable, and cost efficient means to protect sensitive goods from ambient atmosphere. In this presentation we describe the first deposition trials on plastic films with a new PICOSUN™ roll-to-roll (R2R) chamber. This study demonstrated that a thin Al₂O₃ layer deposited with this continuous process enhances the barrier performance of these materials with results similar to those obtained in a non-R2R batch processing module.

Silicon wafers, cellophane, polylactic acid, and polyimide film substrates were coated with Al₂O₃ at 100 °C using both a batch PICOSUN™ reactor and a test setup for a R2R ALD fit to the same reactor. The precursors were trimethyl aluminum and H₂O, and 500 deposition cycles were used. The Al₂O₃ deposited samples were characterized for their barrier and surface characteristics. The deposition rate of Al₂O₃ on silicon wafer was similar for the batch and the R2R ALD processes. The results from the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements in 50 % relative humidity and 23 °C were compared between samples across substrate types and deposition modes. It was found that the R2R chamber provided barrier performance was comparable to traditional batch deposition in several cases, and considerably enhanced relative to uncoated substrates.

The initial mechanical properties of the polymeric substrate were found to be crucial for the barrier properties. For example, an Al₂O₃ coating fabricated on cellophane film was less sensitive to mechanical stresses, and the barrier values obtained were similar to those obtained with batch process for the same substrate. FTIR analyses detected Al₂O₃ covered surfaces after the R2R ALD. AFM images for the batch and R2R produced samples that were quite similar. The relative polarities of surface energy for Al₂O₃ deposited with R2R ALD on all three films were lower than for the batch samples. This indicates some differences in the thin film growth. Implications for manufacturability and scalability will also be discussed.

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3 T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, M. Karppinen, Thin Solid Films 518 (2010) 5463.

9:00am TF+PS-MoM3 An Industrial Approach to Roll-to-Roll Atomic Layer Deposition, *M.J. Söderlund, P.T. Soininen, Ville Malinin*, Beneq, Finland
Spatial ALD method has attracted considerable attention lately as means to increase the throughput and coating area of ALD processes to meet industrial requirements. This interest is driven largely by the superior film quality of ALD thin-films, but also by the other foreseen benefits associated with spatial ALD process (in addition to high process) such as high material utilization efficiency and low maintenance requirement. These benefits, enable by the spatial ALD concept, are coming together today specifically for flexible moisture barrier application, driven by need to improve the quality and reduce the costs of ultra barrier films for moisture sensitive devices (e.g. OLEDs). However, for ALD to break into mainstream in roll-to-roll manufacturing of e.g. various different moisture barrier films, the spatial ALD technological approach should be applicable to a wide range of substrates materials (e.g. polymer, metal, paper), as well as meters wide webs and web thicknesses ranging from tens up to hundreds of micrometers.

This paper describes a scalable roll-to-roll ALD system approach, and presents recent results using a commercial WCS 600 R2R ALD system. The approach is based on relative movement between a web, tensioned on a processing drum, and the spatial ALD coating head, which is in oscillating motion around the central process drum. Process for Al₂O₃ based on TMA and H₂O precursors at 100 C demonstrates growth rates between 0.7 - 1.0 Å/cycle with refractive index higher equal or higher than 1.61. Low non-uniformity of less than 10 % is measured across 480 mm effective coating area. Ultra barrier performance of <5*10⁻⁴ g/(m² day) at 38 C/90 % conditions is demonstrated with only 20 nm thick Al₂O₃ films, made on roll-to-roll basis on 500 mm wide PEN film substrate. Prospects for scaling the technology further in web width and speed are discussed.

9:20am TF+PS-MoM4 Modular Rotating Cylinder Design for Spatial ALD on Porous Flexible Substrates, *Kashish Sharma, R.B. Hall, S.M. George*, University of Colorado at Boulder
Li-ion batteries (LIBs) have a capacity that typically decays versus number of charge-discharge cycles. Surface coatings on LIB electrodes fabricated using atomic layer deposition (ALD) can dramatically improve the capacity stability. The commercialization of these ALD coatings requires the ability to perform ALD on porous battery electrodes on flexible metal webs. In this work, a new spatial ALD (S-ALD) reactor is developed that is based on a modular rotating cylinder design. The outer cylinder remains fixed and contains a series of slits. The slits can accept a wide range of modules that attach from the outside and accommodate precursor dosing, purging or pumping. The inner cylinder rotates (0-200 RPM) and passes underneath the various slits that are spatially separated. This new S-ALD reactor has been characterized using trimethyl aluminum (TMA) and ozone to grow Al₂O₃ ALD films at 40°C on metallized PET substrates. Spectroscopic

ellipsometry measurements obtained Al_2O_3 ALD growth rates of 0.6 -1.1 Å/cycle depending on the O_2 pressure used to prepare the ozone. The Al_2O_3 ALD growth rate was also constant with changing rotation speeds from 60 to 150 RPM. Future experiments will deposit Al_2O_3 ALD films on porous electrodes on flexible metal webs. For these depositions, a "push-pull" design will be utilized where the pressure of the precursor dose will "push" the precursor and carrier gas into the evacuated porous electrode. The reaction products and carrier gas will then be "pulled" from the porous electrode by vacuum pumping. This new spatial ALD reactor has the potential to deposit uniform and conformal thin films on large area and flexible porous substrates at high deposition rates.

9:40am TF+PS-MoM5 Spatial Atmospheric Atomic Layer Deposition of Oxide and Oxysulfide Semiconductors, *Andrea Illiberi**, TNO, Netherlands **INVITED**
Oxide and oxysulfide semiconductors are key components in a wide variety of devices including displays and solar cells. Spatial ALD is emerging as a disruptive deposition technique for the electronic industry because it combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large-area substrates, with high growth rates (up to nm/s) at atmospheric pressure. In this paper we present *spatial atmospheric ALD* of Zn-based multi-component oxides for use as front window in CuInGaSe₂ (CIGS)*solar cells* (i.e. i-ZnO, Zn(O,S), Al:ZnO) and as active channel (i.e. InGaZnO) in *TFT-displays*. Films are grown by sequentially exposing the substrate to oxygen and/or sulfur precursors (H_2O, H_2S) and the metal precursor vapors (i.e. DEZ, TMIn, TEGa, or TMAl). By controlling the kinetics of surface reactions between vaporized precursors and reactive sites at the film surface, the composition of the films can be precisely tuned, achieving a constant concentration-depth profiles of the elements along the growth direction, as measured by EDX and XPS analysis.

CIGS solar cells: The front window of CIGS solar cells consists of a stack of CdS/i-ZnO/Al:ZnO layers. Zn(O,S) is emerging as a successful replacement for the CdS buffer layer, being free of toxic elements and having a wider band gap (> 2.4 eV). Both the [S] and [Al] content in ZnO are accurately controlled in the rage from 0 < [S]/[0] < 1 and 0 < [Al]/[Zn] < 1, enabling the deposition of the entire front window stack by spatial-ALD. The degradation of the electrical properties of Al:ZnO during damp heat test is prevented by a spatial-ALD Al_2O_3 moisture barrier. The use of spatial ALD Zn(O,S)/i-ZnO/Al:ZnO/Al_2O_3 stack as front windows in CIGS cells is being tested.

TFT-displays: InGaZnO (IGZO) has drawn great attention in the display industry over the last few years, because of its high electron mobility (> 10 cm^2/Vs), as compared to the commonly used amorphous silicon. The growth of IGZO has been investigated by Spectroscopic Ellipsometry, while the surface and bulk composition of the films has been measured by Low Energy Ion Scattering and XPS. An initial In-rich phase induces a nucleation phase of about 250 ALD-cycles, followed by film closure. IGZO films have an amorphous structure, as indicated by X-ray diffraction analysis. Spatial ALD IGZO films have been tested as active channel in TFT, achieving a maximum device mobility of 10 cm^2/Vs.

Upscaling: Large area (30 cm wide) spatial ALD of Zn(O,S), Al:ZnO and IGZO will be developed by the roll to roll and sheet-to-sheet technology, respectively, as a new nanomanufacturing platform for the solar and display industry.

10:40am TF+PS-MoM8 Large Area Atmospheric Spatial Atomic Layer Deposition of Zn(O,S) Buffer Layers for CIGS Solar Cells on Glass Substrates, *M.D. Bijker, R.S.R. Archer,* Smit Ovens B.V., Netherlands, *P. Poodt,* Holst Centre / TNO, Netherlands, *A. Illiberi,* Solliance / TNO, Netherlands, *Karel Spee*, Smit Ovens B.V., Netherlands
Spatial ALD (S-ALD) is emerging as a disruptive deposition technique for the electronics and photovoltaics industry because it combines the advantages of ALD, i.e. excellent control of film composition and uniformity, with high deposition rates (up to nm/s) at atmospheric pressure. This allows for a reduction of the Cost of Ownership (CoO) to a level where, for a range of high-volume and low-cost application areas, commercial exploitation is within reach.

S-ALD as developed by the authors makes use of an injector in close proximity (typically less than 100 µm) of a substrate which moves with high speed underneath the injector. This process has been proven to work very well for very flat substrates. Large area glass panels, however, provide quite a challenge as there are large thickness variations over the sheet due to glass thickness variations, surface roughness, bow and warp of the glass. We will present the design and operation of an atmospheric pressure S-ALD sheet-to-sheet tool which can handle 30x40 cm^2 glass panels. The glass

panels enter the system through a load lock, pass two heating zones to fast heat-up the substrates and enter a deposition zone. The glass plates are placed on a super flat susceptor and straightened using a vacuum clamp. Sensors detect the remaining thickness variations of each individual glass plate and adjust the injector head proximity for each glass plate. In high speed the glass plate is moved back and forth underneath the injector. Maximum deposition temperatures are 350°C. The injector is equipped with 7 slots, equipped with injectors for trimethylaluminium (TMA), diethylzinc (DEZ), H_2O and H_2S. Each precursor can be entered independently, but also TMA-DEZ premixing and H_2O-H_2S premixing is possible.

The tool will be used for the deposition of Zn(O,S) buffer layers in CuInGaSe₂ (CIGS) solar cells as an alternative for Chemical Bath Deposition (CBD) of CdS. This replaces an environmentally polluting process with a Cd-free solution. Several authors have reported CIGS solar cells utilizing Zn(O,S) buffer layers with properties very comparable or even somewhat better (+0,5%) to existing CIGS cells using CdS. Cost of ownership (CoO) calculations show that the production cost using S-ALD are also comparable (~\$0,02/Wp).

First Zn(O,S) layers have been prepared using a S-ALD lab-reactor, using DEZ and a mixture of H_2O and H_2S. The composition, optical- and electrical properties of the films can be continuously controlled by different H_2O/H_2S mixing ratios from ZnO. Further experiments are ongoing, including the deposition of Zn(O,S) buffer layer in full CIGS solar cells and its effect of solar cell performance.

11:00am TF+PS-MoM9 Growth Rates and Mechanisms for Al_2O_3 ALD using TMA/ O_3 at Atmospheric Pressure, *MoatazBellah Mousa, C.J. Oldham, G.N. Parsons*, North Carolina State University
Under typical low pressure ALD conditions, ozone (O_3) is reported to speed up ALD processes compared to water-based reactions because shorter purge times are needed to fully desorb ozone O_3. Many high-throughput ALD processes are designed to operate at atmospheric pressure where viscous fluid transport can have significant effects. We developed an ALD process using trimethyl aluminum (TMA) and O_3 in a variable-pressure flow tube reactor and measured growth rates, film composition and film uniformity in the growth zone for pressures between ~2 Torr and 760 Torr and temperature ranging from 70°C to ~250°C. We also adjusted overall gas flow rate to study the role of gas residence time. Film thickness was determined by ellipsometry and growth was monitored using an in-situ Quartz Crystal Microbalance (QCM). We observe self-limiting growth between ~150 °C and 250 °C at both ~2 Torr and 760 Torr, and larger growth rate at lower temperature. At high pressure the growth rate is ~20% larger than at low pressure, which is ascribed to slower transport of desorbing product species through the boundary layer at high pressure. We also find that longer O_3 exposure times are needed compared to low pressure growth. This is consistent with a model for the ozone dissociation kinetics showing that higher pressure enhances the rate of ozone loss. The ozone depletion also predicts an observed gradient in film growth rate under sub-saturation conditions along the length of the reactor. During TMA/O_3, O insertion leads to surface methoxy and formate groups at low temperature, whereas surface hydroxyls form at higher temperature. In our reactor, QCM analysis shows evidence for this temperature-dependent surface reaction mechanism at 2 Torr, and it persists at 760 Torr under saturated conditions. Under saturated growth conditions, TOF-SIMS analysis shows films deposited at 2 Torr and 760 Torr have similar composition, with some extra carbon contamination at higher pressure. Overall, similar ALD growth can be achieved for TMA/O_3 at 760 Torr and ~2 Torr, where care must be taken to take into account the faster rate of O_3 dissociation at higher pressures, especially at higher temperature.

11:20am TF+PS-MoM10 Integration of Feature and Reactor Scales during the Simulation of ALD Scale Up, *Angel Yanguas-Gil, J.A. Libera, J.W. Elam*, Argonne National Laboratory
As the number of ALD processes, materials and applications increase, it is becoming increasingly important to develop the ability to screen and identify the most prominent candidates for scale up. Precursor pressure, reaction probability, ideality of the surface chemistry, but also other considerations like throughput, surface area, and materials utilization, are critical factors that will determine the feasibility of a particular process. In particular, there are three questions that need to be answered in the transition from lab-scale to manufacturing: 1) what is the impact of a particular precursor chemistry, 2) what are the best processing conditions for a given precursor and substrate, 3) what is the optimal reactor design?

In this talk we will focus on the issue of predicting the scalability and fundamental economics (throughput, precursor utilization) of lab-scale ALD processes. Our approach, developed as part of our work on process development and scale up, combines the experimental characterization of ALD processes in bench-scale reactors, the use of simple analytic models, and the development of new 3D multiscale simulation tools that are

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* Paul Holloway Award Winner

optimized to the conditions typically found under ALD conditions, including providing simulated quartz crystal microbalance and mass spectrometry data at any point of the reactor.

Our code, based on open-source libraries, is able to incorporate high-surface area substrates on reactor scale simulations for both cross-flow and roll-to-roll processes, and it takes advantage of the ALD surface chemistry to achieve an extremely efficient two-way coupling between reactor and feature length scales. This method is based on a new approach to simulate feature scale coating that essentially provides the infinite trajectory-limit of the Monte Carlo simulations typically used in the literature.

Besides the description of the model and its implementation, we will exemplify our methodology by presenting results of different metal oxides by ALD, including the validation of the code in a large area reactor. We will also show the results of a parametric study on the impact of non-ideal surface chemistry as well as the presence of high surface area materials / nanostructured features on the substrate. According the results obtained, the presence of high surface area materials makes continuum ALD processes like R2R more efficient. This is a consequence of a more general result of our parametric study, which shows that high reaction probabilities play an important role in ALD scale up.

Plasma Science and Technology
Room: 308 - Session PS-MoA

Advanced FEOL/Gate Etching
Moderator: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

2:00pm PS-MoA1 Breaking Through Limits in Semiconductor Technology, *Chang-Jin Kang*, Samsung Electronics, Republic of Korea **INVITED**

[Abstract]

Our current IT industry, which possesses a strong demand of personal mobile devices, is accelerating towards smart devices with the convergence of new technologies.

Under these circumstances, the development of semiconductors with high speed, high density, low power and high reliability are crucial. Scaling down of devices and to ensuring cost-effective technologies are the two most important tasks the semiconductor industry is facing.

To find proper solutions for the development of future devices and to overcome the limitations of current technologies, mid and long-term projections of future silicon technology as well as DRAM, NAND and Logic technology trends will be covered.

2:40pm PS-MoA3 Mechanism of Silicon Damage during N_2/H_2 Block Etching for FinFET CMOS, *Tamotsu Morimoto*, Tokyo Electron Limited, Japan, *H. Ohtake,* Tokyo Electron America, Inc., *T. Wanifuchi*, Tokyo Electron Miyagi Limited, Japan

In this study, we found that the degradation of a silicon active area during N_2/H_2 block etching strongly depends on ion energy and flux because ions generate significant damage on the silicon surface as compared with the damage to the active area due to hydrogen radicals.

Plasma-induced damage on Si substrates has become a serious concern in CMOS fabrication processes. In addition, the appearance of Fin-FETs have made it necessary for plasma etching processes to use masks made by the organic film opening process and block etching in order to implant the P- or N-type regions. In this study, part of the fin structure was exposed to plasma during organic block etching. It was found that the source and drain regions of the fin area were damaged. However, the impact of the generated damaged layer on the electrical properties has not been clarified, especially junction leakage of the source and drain. In this paper, effect of etching using N_2/H_2 gas combination on p–n junction leakage current at reverse bias was investigated. Parameters of the N_2/H_2 plasma like flow rate, etching time, peak-to-peak voltage of the RF bias (V_{pp}), and the micro wave power (MW) were varied. Si substrate with a p–n junction was exposed to the N_2/H_2 plasma, followed by nickel silicidation to enable electrical characterization.

Junction leakage current increased by increasing V_{pp} and reducing MW for fixed etching times and was independent of the hydrogen ratio in the N_2/H_2 gas. This indicates that ion has a stronger influence on Si damage than H_2 radicals. With etching depth kept fixed, a high hydrogen ratio showed less damage because etching rate was higher. In addition, we obtained smaller damage for higher V_{pp} at constant MW because etching time was shorter owing to the high etching rate. Accordingly, we can infer that ion energy and cumulative ion flux have a significant impact on the degradation of the p–n junction. From the transmission electron microscopy analysis, the damaged layer, which degraded Si crystallinity, became thicker by increasing the exposure time of the Si substrate to the N_2/H_2 plasma. Most probably, the damaged layer has a lot of defect sites which act as trap sites beside the junction, which in turn causes the p–n junction leakage current to increase.

We found that the ratio of ion/radical in the plasma should be lower to reduce the damage of silicon active area by N_2/H_2 block etching. High etching rate and low V_{pp}, which correspond to high hydrogen ratio and low RF bias, is the best combination for low-damage organic block etching.

3:40pm PS-MoA6 Plasma Etch in the Era of Atomic Scale Fidelity, *Vahid Vahedi, J. Marks*, Lam Research Corp **INVITED**
The ultimate goal of IC manufacturing is to produce the structures that are conceived and modeled by design engineers in the real world with high fidelity. We choose the term "fidelity" deliberately to express that what is needed in the end is the highest possible degree to which a material structure matches the design intent. It includes but is not limited to statistical criteria such as accuracy and precision.

Plasma etch plays a key role in obtaining structural fidelity in all three dimensions. Precision is obtained by means of wafer- to- wafer, chamber- to- chamber and tool- to- tool matching. Accuracy on the other hand requires control of proximity and 3D effects such as critical dimension (CD) loading, profile loading, aspect ratio dependent etching (ARDE), and selectivity.

As we approach devices with a half pitch of 10 nm and below, atomic scale fidelity is required because the device dimensions and their allowed tolerances are of the same order of magnitude as the inter-atomic distances in the crystal lattice. This type of performance can be obtained when the material is removed layer by layer. The etch process is comprised of single unit steps which repeat in cycles. Each step uses the simplest possible chemistry to surgically target specific reactions at the wafer surface such as activation, removal, and passivation. We call this layer- by- layer etch with atomic fidelity Atomic Layer Etchatomic layer etch1.

In this presentation, we introduce the framework of high productivity, production- worthy ALE atomic layer etch and the implications for hardware and process development. Results for both dielectric and conductor etch obtained with Lam's Research' latest etch products will be presented.

References:

1. Kanarik, et al., Solid State Technology, (2013) 14-17.

4:20pm PS-MoA8 Challenges of 3D NAND Staircase Patterning Process, *Hui Zhou*, *S. Srinivasan, J. Choi, A. Khan, L. Yu, Z. Yao, A. Agarwal, S. Rauf*, Applied Materials Inc.
NAND memory microfabrication is at the transition point to vertical structures. A variety of 3D NAND device designs have been reported, such as bit cost scalable (BiCS) and terabit cell array transistor (TCAT). Despite the difference in the structures and operational mechanisms of 3D NAND devices, the microfabrication processes share a common first step, the formation of the landing pads for the control gate via contacts. The "staircase" of pad landings is realized by alternating film etching and resist trimming. To ensure high yield, the registration for the vias must be ensured by the insitu staircase patterning process with CD uniformity being the most critical figure of merit for desired yield. CD uniformity is most sensitive to the resist trimming process and is controlled by plasma distribution and electrostatic chuck temperatures. Local CD non-uniformity may originate from microloading effect or asymmetry impact, and the approaches to improve the local CD uniformity focus on mitigating loading and reducing the asymmetry with process and hardware development, that are also supported by quantitative modeling results. Early versions of the staircase patterning process resulted in low throughput due to multiple resist trimming steps. High throughput is required to reduce the cost of fabrication. Power, flow, and pressure are effective knobs in improving the resist trimming rate. Reducing the gas transition time and using continuous plasma between different gas has also proven effective for further improving throughput. Challenges and progress for 3D NAND staircase patterning process will be discussed, and innovative hardware and process solutions will also be presented.

4:40pm PS-MoA9 Impact of the Addition of $SiCl_4$ in a $CH_3F/O_2/He$ Chemistry for the Nitride Spacer Etching of FDSOI 14 nm Technology, *C. Arvet, S. Lagrasta, Maxime Garcia Barros*, STMicroelectronics, France, *S. Barnola, N. Posseme,* CEA, LETI, MINATEC Campus, France, *F. Leverd*, STMicroelectronics, France
Today, the choice of chemistry for nitride spacer etching is a CH3F/O2/He based chemistry. But such chemistry leads to 10A and 15A silicon and silicon germanium consumption, respectively. Furthermore the remaining carbon at the silicon or silicon germanium surface can lead to a poor silicon surface quality which does not allow the film regrowth. The optimization of this process is not enough reliable in order to be used in production for the FDSOI 14 nm technologies.

In this context, we investigated the impact of SiCL4 addition to CH3F/O2/He/CH4 chemistry.

Ellipsometry measurements performed on blanket silicon nitride and silicon germanium film allow us to investigate two essential points for the FDSOI 14 nm technologies:

-The resist consumption

-The opportunity to obtain an infinite selectivity of silicon nitride to silicon germanium.

Complementary XPS and FTIR analyses have been performed for a better understanding of the etch mechanisms and will be presented.

These results have been confirmed on patterned structures. TEM analyses have shown no silicon germanium recess with no foot formation after silicon nitride spacer etching and wet cleaning. Finally, the compatibility of this new etch chemistry on epitaxial growth quality will also be presented.

5:00pm PS-MoA10 Hydrofluorocarbon Gases for Selective, Low-Damage, Silicon Nitride Etching, *James Royer*, *R. Gupta, V. Pallem*, American Air Liquide

Maintaining Moore's law has introduced increasingly stringent process requirements for front-end device technologies. These requirements create considerable technical challenges for silicon nitride gate spacer etching. Etch processes must remove thin silicon nitride layers while maintaining stringent physical constraints and chemical integrity of the underlying substrate. Therefore, the etch gases must be tailored with appropriate functionality for selective silicon nitride etching. This study presents hydrofluorocarbon (HFC) etch gases which demonstrate selective etching of silicon nitride with respect to silicon oxide, and poly-silicon. Using a RIE plasma etch tool, the performance of each molecule is studied on blanket wafers and analyzed using spectroscopic ellipsometry, x-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Etch rates and selectivities for each HFC are evaluated over a range of O_2 flow to determine the desirable process windows. Select HFCs have large process windows with infinite silicon nitride to poly-silicon selectivity due to fluorocarbon deposition on the poly-silicon. The fluorocarbon deposition layer on poly-silicon inhibits undesired silicon-carbide or silicon-oxide formation. XPS surface analysis and depth profiling shows a reduction in carbon and oxygen incorporation in poly-silicon compared to similar processes using the industry standard molecule, fluoromethane.

5:20pm PS-MoA11 Alternative Process for Thin Layer Etching: Application to Nitride Spacer Stopping on Silicon Germanium, *Nicolas Posseme*, *G. Santini, O. Pollet, C. Arvet, S. Barnola*, CEA-LETI, France

Today, minimizing the so-called silicon germanium (or silicon) recess during nitride spacer etching is extremely difficult to achieve but mandatory since it directly impacts the device performances. Despite of etch chemistry or tool improvement, this silicon germanium recess is only limited.

In this context, we proposed an alternative etching process to overcome these issues and meet the highly complex requirements imposed by device fabrication processes. This new etching process is based on two steps. In a first step, the film is modified in volume by a H_2 plasma performed in a conventional etch tool (ICP or RIE) followed in a second step by a selective removal of the modified layer with respect to the non-modified material.

In this study, we will present this alternative process for nitride spacer etching stopping on silicon germanium for FDSOI devices. It will be demonstrated that the silicon nitride film modification can be adjusted by playing on plasma parameters. XPS and infrared spectroscopy analyses have been performed on blanket silicon nitride film to understand the silicon nitride film modification induced by H_2 plasma . These mechanisms of the silicon nitride film damage will be discussed.

In the meantime, different approaches (dry or wet) to remove the modified silicon nitride film without non-modified nitride or silicon germanium films consumption have also been investigated. The advantages and the drawbacks of these approaches will be presented.

Starting from the best process conditions (modification and removal steps), TEM analyses performed on patterned structures have revealed that the silicon germanium recess is less than 5A for a wide range of nitride film over etch (from 30 to 120%) with no foot formation compared to more than 15A recess and 20 A foot formation using the best current etching processes (CH_3F/O_2/He chemistries targeting 50% over etch).

Finally, the compatibility of this new nitride spacer etching process on SiGe epitaxial growth quality will also be presented. It will be shown, that the clean surface obtained after the modified nitride film removal leads to a perfect epitaxial growth for different silicon nitride over etch from 30 to 120%.

Advanced Surface Engineering
Room: 302 - Session SE+PS+TF-MoA

Pulsed Plasmas in Surface Engineering
Moderator: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology

2:00pm SE+PS+TF-MoA1 Complex Magnetic Systems for High Power Pulsed Magnetron Sputtering, *Priya Raman**, *I.A. Shchelkanov, J. McLain*, University of Illinois at Urbana Champaign, *S. Armstrong*, Kurt J. Lesker Company, *B. Zhang, M. Schilling*, DEXTER Magnetic Technologies, *D.N. Ruzic*, University of Illinois at Urbana Champaign

High Power Pulsed Magnetron Sputtering (HPPMS) is a type of magnetron sputtering technique where high peak power pulses reaching tens of kilowatts are applied to the sputter magnetron target keeping the average power equal to that of direct current magnetron discharges by using low duty cycles. Due to very high power densities, HPPMS discharge leads to high degree of ionization of the sputtered material. These ionized sputtered materials assist in film growth leading to more adhesive, dense, and smoother films. Therefore, HPPMS is considered an ideal candidate for the next generation magnetron sputtering systems, however these techniques suffer from low deposition rate due to "return effect" of the ionized sputter material [1]. One way to solve this problem is to have a magnetic field configuration that is optimized for HPPMS discharges. Magnetic pack design is critical as it helps in achieving full-face target erosion and higher deposition rate in HPPMS. Magnet pack design is generally selected by experimental observation. It has been confirmed from our previous work on HPPMS that a spiral-shaped magnetic field design on 14 inch (36 cm) diameter copper target was able to produce superior plasma uniformity on the substrate in addition to improved target utilization without the need for magnet rotation [2]. Commercial 4 inch (10cm) magnetron sputter guns function with a variety of power supplies like DC, Pulsed-DC, Modulated Pulsed Power Magnetron sputtering (MPP) and HPPMS. These 4 inch magnetron sputter guns typically have a conventional circular magnetic field configuration and suffer from low deposition rate in HPPMS discharges. To optimize the magnet field configuration in HPPMS for the 4 inch magnetron sputter gun, the spiral design from the 14 inch target was scaled down and modified to fit into 4 inch magnetron sputter gun. A new "ε" design magnet pack with enhanced discharge parameters was developed by modifying the spiral magnet pack in COMSOL Multiphysics, which leads to higher deposition rate and better target utilization in HPPMS compared to the conventional magnet pack. The influence of "ε" design magnet pack configuration on deposition rate, plasma parameters, and discharge stability with HPPMS (Huettinger's HiPIMS), MPP(zPulser), DC and pulsed DC power supplies were investigated. The deposition rate for "ε" pack is 2.1±0.2 times the conventional pack for an average discharge power of 500W with zPulser power supply.

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2:20pm SE+PS+TF-MoA2 Triple Langmuir Probe and Ion Fraction Measurements in an Industrial PVD Deposition System, *YuiLun Wu*, *S.S. Ma, I.A. Shchelkanov, D.N. Ruzic*, University of Illinois at Urbana-Champaign

High Power Pulsed Magnetron Sputtering (HPPMS) discharges are an ideal candidate for the next generation PVD magnetron sputtering systems. Compared with traditional DC sputtering, HPPMS discharges offer high degree of ionization of the sputtered material with very high peak power on the target. An industrial size chamber will be used to investigate the HPPMS discharge operation in full scale production environments utilizing different power supplies. Plasma was observed to be originated from the race track region then expanded downward afterwards. Plasma density was very high (~10^{19}-10^{20} m^{-3}) when generated then decreases as it expanded [1] In order to understand the temporal evolution of the plasma between the target and the wafer plane, a time resolved triple Langmuir probe was employed to measure the plasma parameters such as electron temperate and density and scanning in a three dimensional map. Plasma parameters between traditional DC discharge and HPPMS discharge will be compared. Quartz crystal microbalance and 2 inch gridded energy analyzer will be designed to determine fluxes of metal ions, metal atoms and argon ions. The setup will be able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the HPPMS discharge.

* Coburn & Winters Student Award Finalist

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2:40pm SE+PS+TF-MoA3 Understanding the Physics of Magnetron Discharges: Ionization Zones and Their Role in Transport of Charged Particles, *Matjaž Panjan, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory **INVITED**

Magnetron sputtering is one of most commonly used techniques for the deposition of thin films. The physics of magnetron discharges has been intensively studied, however, recent investigations revealed that our understanding is rather incomplete. To the naked eye the ionization process appears to be homogeneously distributed along the racetrack – i.e. the region of strongest target erosion caused by sputtering. Imaging of the magnetron discharges with intensified CCD cameras using short exposure times revealed differently, namely, the plasma is concentrated in several zones along the racetrack [1-3]. These so-called ionization zones or spokes are organized in periodic or quasi-periodic patterns that move in the $\mathbf{E} \times \mathbf{B}$ direction with approximately 1/10 of the electron drift speed (where $\mathbf{E}$ and $\mathbf{B}$ are the electric field and magnetic field vectors). Recent experiments further revealed that ionization zones are a fundamental feature of magnetron discharges run in pulsed and continuous mode [4]. In this talk, recent advances in understanding the ionization zone phenomenon will be reviewed. The interpretation of the formation, drift, self-sustainability, and self-organization of ionization zones will be presented with emphasis on potential, electric field and ionization rate distributions. It will be shown that ionization zones play a critical role in the transport of both electrons and ions [4-6].

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[2] A. Anders et al., J. Appl. Phys., 111 (2012) 053304

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3:40pm SE+PS+TF-MoA6 Properties of Ionization Zones in Magnetron Sputtering Observed in the Transition Region between dc and HiPIMS, *André Anders, Y. Yang, J. Liu, Y. Qiu*, Lawrence Berkeley National Laboratory

Research in the last years revealed that the plasma in high power impulse magnetron sputtering (HiPIMS) is rich in structure, featuring self-organized patterns [1], plasma flares [2], and azimuthally asymmetric particle jets [3]. Most prominent are drifting regions of enhanced excitation and ionization, which are called ionization zones but sometimes also labeled spokes in analogy to similar phenomena seen in other $\mathbf{E} \times \mathbf{B}$ devices such as Hall thrusters. Fast imaging of ionization zones in HiPIMS revealed the presence of several distinct ionization zones, for example 3-5 zones in the case of sputtering with a 3-inch magnetron at peak currents of the order 100 A. The zone drift velocity is several 1000 m/s, up to 10^4 m/s, yet much slower than the $\mathbf{E} \times \mathbf{B}$ drift of electrons, which is of the order of 10^5 m/s. In contrast, when sputtering continuously (dc) at very low current (less than 1 A), and at low pressure (less than 1 Pa), we find only one ionization zone moving at low velocity in the reverse, i.e. the $-\mathbf{E} \times \mathbf{B}$ direction. Increasing the current and pressure tends to split the zone into two and occasionally three zones. The appearance of each zone depends on current and other factors such as the pressure of the process gas. In this contribution, we explore the transition regime between dc operation at low current and HiPIMS operation with high peak currents. Using fast streak and frame imaging cameras we detect even more structures and structure changes than anticipated. We conclude that the discharge and its particle transport is governed by zone-related instabilities and turbulence.

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[2] P.A. Ni, et al., Appl. Phys. Lett. 101 (2012) 224102.

[3] M. Panjan, et al., Plasma Sources Sci. Technol. 23 (2014) 025007.

4:00pm SE+PS+TF-MoA7 Observation of Multiple Charge States and High Ion Energies in High-Power Impulse Magnetron Sputtering (HiPIMS) and Burst HiPIMS using a LaB$_6$ Target, *Robert Franz*, Montanuniversität Leoben, Austria, *C. Clavero*, Lawrence Berkeley National Laboratory, *R. Bolat*, Nazarbayev University, Kazakhstan, *R. Mendelsberg, A. Anders*, Lawrence Berkeley National Laboratory

In high-power impulse magnetron sputtering (HiPIMS), a variation of pulsed magnetron sputtering, short high-voltage pulses are utilized to create discharges with high current densities and a high degree of ionization of the

target atoms. In recent years, more complex pulse patterns than the single pulses used in the original or conventional HiPIMS have been developed, e.g. burst-HiPIMS where a series of very short (few μs) pulses are bunched to form bursts.

In the present work, the charge-state-resolved ion energies of HiPIMS discharges were measured, using a LaB$_6$ target, as a function of charging voltage, pulse length, pulse frequency and on/off time ratio within applied HiPIMS bursts [1]. The highest charge states can reach +2 and +3 for boron and lanthanum ions, respectively. At high discharge powers, the B/La ion ratio can exceed the respective atom ratio in the target producing B-rich plasma with up to 98% boron ions. In the case of two-segmented bursts with high on/off time ratios, La^{3+} is the dominating lanthanum ion species and the ion energy distribution of B$^+$ shows a pronounced high-energy tail extending up to 750 eV. The measured plasma compositions, ion charge states and ion energies are discussed within the established framework of HiPIMS discharges and the recent postulation that potential humps are associated with drifting ionization zones. The recorded high B/La ion ratios are a result of complex effects related to particle fluxes in the HiPIMS plasma of compound targets, as explained with the help of an expanded schematic representation of self-sputtering and gas atom recycling. The high energies of the B$^+$ ions are based on a combination of the self-sputtering of boron, backscattering of incident boron ions on lanthanum atoms in the target and acceleration by localized potential humps [2]. Further evidence for potential humps is provided by the observed charge-state dependence of ion energies and features between the thermal peak and high-energy tail of the ion energy distribution functions.

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[2] A. Anders, M. Panjan, R. Franz, J. Andersson, P. Ni, Appl. Phys. Lett. 103 (2013) 144103.

4:20pm SE+PS+TF-MoA8 Pulsed Magnetron Sputtering of Novel Multifunctional Films, *Jaroslav Vlcek, J. Rezek, J. Kohout*, University of West Bohemia, Czech Republic

High-power impulse magnetron sputtering with a pulsed reactive gas flow control was used for the reactive deposition of Ta-O-N films with tunable composition and properties [1]. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Ta target in Ar-O$_2$-N$_2$ gas mixtures at an average target power density of up to 2.4 kWcm^{-2} in a pulse. The repetition frequency of pulses was 500 Hz at a fixed 50 μs voltage pulse length and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to adjust the film composition from Ta$_2$O$_5$ to a mixture of Ta$_3$N$_5$ and TaN. We prepared Ta-O-N films possessing appropriate band-edge levels for water splitting and a narrow optical band gap of 2.5 eV that permits a visible light absorption up to 500 nm.

Pulsed dc magnetron co-sputtering of a single target (B$_4$C-Si, B$_4$C-Zr or B$_4$C-Hf-Si) in Ar-N$_2$ gas mixtures was used for deposition of different multifunctional films. The repetition frequency of pulses was 10 kHz at a fixed 85 μs voltage pulse length and the total pressure of 0.5 Pa. We present the results obtained for amorphous Si-B-C-N films with an exceptionally high thermal stability (above 1500°C) and very high optical transparency [2], for nanostructured Zr-B-C-N films with a high hardness (37 GPa) and high electrical conductivity [3], and for nanostructured Hf-B-Si-C films with a high hardness (34-37 GPa), high electrical conductivity and significantly improved oxidation resistance in air up to 800°C [4].

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[3] J.Vlcek, P.Steidl, J.Kohout, R.Cerstvy, P.Zeman, S.Proksova, V.Perina, Surf. Coat. Technol. 215 (2013) 186.

[4] J.Kohout, J.Vlcek, J.Houska, P.Mares, R.Cerstvy, P.Zeman, M. Zhang, J.Jiang, E.I. Meletis, S. Zuzjakova, Surf. Coat. Technol. (submitted).

4:40pm SE+PS+TF-MoA9 Surface Engineering of Magnesium and Magnesium Alloys for Improved Corrosion Resistance, *Michael Melia, J.R. Scully, J.M. Fitz-Gerald*, University of Virginia

Due to the need for significant weight reduction of structural components, the development of Mg alloys has been ongoing over the last 100 years. One long-standing obstacle regarding the use of Mg alloys for widespread field application is their intrinsically poor corrosion resistance and lack of surface films or oxides that enable "self-healing" or active scratch protection. Micro-galvanic induced "self-corrosion" due to alloy heterogeneity is a key concern. The effects of Excimer laser surface modification and electric arc surface processing on the corrosion resistance of commercially pure Mg (99.8 wt% Mg) and Mg alloy (AZ31B) is

investigated. Non-equilibrium processing is being investigated to control surface chemistry, microstructure, and phase formation in order to mitigate the micro-galvanic corrosion with the initial goal of microstructural and composition homogenization. In an attempt to achieve surface homogenization and control Mg evaporation, a range of operating parameters (energy density, dwell time, and processing atmosphere) were explored.

Surface morphology, composition, and local phase imaging were performed with scanning electron microscopy in secondary and backscattered electron imaging modes. X-ray diffraction was used to examine phase and surface regions in grazing incidence mode. Corrosion characterization was performed in a standard three electrode corrosion cell with an aerated 0.6 M NaCl solution. Electrochemical Impedance Spectroscopy (EIS) (10,000 to 0.001Hz) and potentiodynamic polarization scans (0.1 mV/s) were used to determine corrosion resistance, anodic/cathodic behavior, pitting potential and open circuit potential (OCP).

Preliminary results confirm that a measured level of surface homogenization was achieved irrespective of process gasses used (Ar, N_2, He). Moreover, in the case of N_2 processed 99.8% purity Mg samples, the formation of Mg_3N_2 was found to have a significant impact on the corrosion resistance. The AZ31B samples processed in Ar exhibited a similar corrosion response to the N_2 processed surfaces, suggesting homogenization was a larger factor than nitriding. The cathodic behavior consistently exhibited a significant reduction in the rate of the H_2 evolution reaction, more apparent in 99.8% purity Mg. Furthermore, the OCP was reduced by 100-350 mV. Impedance results support these findings with a significant improvement in polarization resistance after treatment. However, processed samples exhibited a minimal change in anodic behavior besides minor fluctuations in pitting potential. Possible mechanisms for the inhibition of the cathodic reaction rate will be presented and discussed.

5:00pm SE+PS+TF-MoA10 Designing a Precious Metal-Free Catalyst for Purification of Automotive Exhausts: NO Reduction and CO Oxidation on CuO(110) Surface, *H. Kasai, J. Moreno, A.A. Padama,* Osaka University, Japan, *C. Matsuda, K. Naito, M. Uenishi, H. Tanaka,* Daihatsu Motor Co., Ltd, Japan, *Y. Nishihata,* Japan Atomic Energy Agency, Japan, *Mamoru Sakaue*, Osaka University, Japan

Nitrogen oxide (NO_x) and carbon monoxide (CO) are known by-products of fossil fuel combustion, which greatly contribute to atmospheric pollution. Thus, understanding the conversion process of NO_x and CO into less hazardous gases is of utmost importance. It is well known that precious metals (such as Rh, Pd and Pt) work well to reduce these pollutant gases, but their high cost is a road block to a more prevalent use. Therefore, a more readily available and inexpensive material with comparable, if not better, catalytic performance is needed. Our group has investigated the role of surfaces as a foundation to realizing designer materials, in this case for exhaust purification [1]. In particular, we have previously studied the dissociation of nitric oxide (NO) on $Cu_2O(111)$ surface [2-4]. In this work, we look at the possibility of using a CuO catalyst for NO reduction and CO oxidation. Using density functional theory, we first investigated the dissociation process of NO on CuO(110) surface [5]. We found that NO is molecularly adsorbed perpendicular to the surface on the active hollow site between the surface Cu-atoms with an N-end configuration. An energy barrier of 1.1 eV was obtained for NO dissociation. The dissociated state was found to be most stable when the coadsorbed N and O atoms are on adjacent hollow sites. In comparison with the Rh(111) surface, the CuO(110) provides lower activation barrier for NO dissociation and lower adsorption energies for coadsorbed N and O atoms. To further investigate the oxidation of CO after the NO dissocation process, CO was adsorbed on the CuO(110) surface with coadsorbed N and O atoms. In this case, CO was molecularly adsorbed on top of a surface Cu atom while attracting the adsorbed O atom. An energy barrier of 0.9 eV was obtained for the CO oxidation process. This barrier was lower than the case of CO oxidation on Rh(111) surface with adsorbed oxygen atoms. The resulting CO_2 molecule was stably adsorbed with its center on top of a surface Cu atom. The results obtained in this study are in agreement with our experimental findings. In conclusion, we believe that CuO is a very promising catalyst for the purification of automotive exhausts.

Thin Film
Room: 307 - Session TF+PS-MoA

ALD Surface Reactions and Precursors
Moderator: Andrew Cavanagh, University of Colorado, Boulder

2:00pm TF+PS-MoA1 Broadband Sum-frequency Generation: Studying the Initial Growth of ALD Al_2O_3 by Nonlinear Surface Vibrational Spectroscopy, *Vincent Vandalon, R.H.E.C. Bosch, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The understanding of the atomic layer deposition (ALD) processes has advanced significantly through the insight obtained with in situ linear vibrational surface spectroscopy, in particular by Fourier transform infrared (FTIR) spectroscopy. In this work we apply a nonlinear vibrational spectroscopy technique, the so-called broadband sum-frequency generation (BB-SFG) method, to study the ALD surface chemistry in situ. BB-SFG is a laser based technique, new to the field of ALD, in which a short visible spectrally-narrow laser pulse (~1 ps) is combined with an ultrashort broadband IR pulse (~90 fs) impinging simultaneously on the sample. The generated sum-frequency spectrum, detected in the visible, contains a part of the vibrational fingerprint of the IR region (bandwidth ~100 cm-1) which can detected "background-free" with a high sensitivity even at short integration times (1-100 s). Moreover, the surface selective nature of BB-SFG is uniquely suited for the study of the ALD surface chemistry in which the surface groups can be monitored accurately. In this presentation, first the BB-SFG method developed in our group in the last few years will be explained. Subsequently, the application of the method during ALD Al_2O_3 (from Al(CH3)3 and H2O) will be addressed. In particular the initial film growth of Al2O3 on H-terminated Si(111) will be followed by probing the Si-H stretch mode (2084 cm-1) with BB-SFG. The decrease in Si-H signal due to Al(CH3)3 and H2O exposure will be correlated with the increase of the second-harmonic signal [1], revealing insight into the kinetics of initial film growth as well as the surface chemistry during steady-state growth. The results will be combined with observations by FTIR studies from our own work and from literature [2]. The surface reactions during the initial growth of Al2O3 by ALD will be addressed.

References:

[1] Höfler, APPL PHYS A-MATER 63, 533-547, 1996

[2] Frank, Chabal, Wilk, APL 82, 4758, 2003

2:20pm TF+PS-MoA2 *In Situ* FTIR Analysis of Reaction Mechanisms between Trimethylaluminum and Carbonyl-Containing Polymers During ALD, *Philip Williams, E.C. Dandley, A. Brozena, C. Needham, C.J. Oldham, G.N. Parsons*, North Carolina State University

New methods to modify polymers are of interest for numerous applications. The chemical mechanisms during trimethylaluminum (TMA) and water exposure during Al_2O_3 ALD onto polymers depends strongly on the polymer substrate and ALD conditions. Under some conditions, a solid oxide film can form with a relatively abrupt polymer/oxide interface. Typically however, TMA can diffuse sub-surface and react with the polymer in the substrate near-surface or bulk. Recently, we studied mechanisms during TMA vapor infiltration into various polymers using *in situ* infrared spectroscopy. In many polymers, the TMA coordinates with a polymer functional group, either on the backbone or on a side-chain, to form a Lewis acid/base adduct. For example, in poly(vinylpyrrolidinone) (PVP), the carbonyl of the amide moiety (~1780 cm^{-1}) is observed to coordinate strongly with trimethylaluminum and shift to ~1725 cm^{-1}, and the adduct remains stable until water exposure. After water treatment, the adduct mode decreases and the original amide carbonyl signal appears to return. This could indicate release of TMA, but aluminum oxide formation in the polymer shows clearly that the TMA reacts within the polymer. Ab initio calculations (B3LYP) were performed to support mechanistic analyses of TMA within the polymer. A similar TMA/carbonyl adduct formation/release mechanism is observed during TMA/water exposure to poly(methyl methacrylate). On the other hand, when poly(acrylic acid) is exposed to TMA, the carbonyl mode disappears then does not reappear after water exposure. This suggests that in PAA, the TMA reacts with the carbonyl to form a stronger covalent bond that does not change upon water exposure. This difference in reactivity for TMA in the polyacid is likely associated with the presence of acidic hydrogens aiding in the formation of the methane byproduct and more stable covalent aluminum-oxygen bonds. These results help expand understanding of ALD onto polymers and can enable better control of coating and infiltration processes.

2:40pm TF+PS-MoA3 Time-resolved FT-IR Spectroscopy during ALD using La(^{i}PrCp)$_3$ and H$_2$O, *Brent Sperling, J.E. Maslar, W.A. Kimes,* NIST

In situ Fourier transform infrared (FT-IR) spectroscopy has provided many valuable insights into various chemistries used for atomic layer deposition (ALD). Frequently, it is used to observe the molecular fragments remaining on a surface after exposure to each precursor or the phonon modes of films as they are deposited layer-by-layer. The limitations of FT-IR spectroscopy, however, have restricted it to quasi-static conditions that differ dramatically from most growth studies. Spectra cannot easily be obtained with the temporal resolution needed to keep pace with typical ALD cycle times. We have developed a method that signal averages time-resolved spectra over multiple ALD cycles to improve the rate of data acquisition to around 150 ms. Additionally, by using external reflection from a metal surface, absorption by surfaces species is enhanced; alternating polarization states allows the surface to be differentiated from gas-phase species and deposition on the windows. We apply this method to La(^{i}PrCp)$_3$/H$_2$O chemistry (^{i}PrCp = isopropyl-cyclopentadienyl), which has proved to be difficult to understand from growth studies. We present our attempts to recreate literature conditions in our laminar flow reactor with *in situ* FT-IR spectroscopy to observe surface and gas-phase species.

3:00pm TF+PS-MoA4 Surface Reactions and Interface Evolution during the ALD of HfO$_2$ on GaAs Surfaces Studied by *In Situ* ATR-FTIR, *Liwang Ye, T. Gougousi,* University of Maryland, Baltimore County

In situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was utilized to study the surface reactions and interface evolution during the Atomic Layer Deposition (ALD) of HfO$_2$ on GaAs(100) surfaces. The chemistry studied involves the use of tetrakis (dimethylamino) hafnium (TDMAH) and H$_2$O. The experiments were performed on chemical oxide and HF etched GaAs(100) starting surfaces. For the deposition of HfO$_2$ on chemical oxide GaAs surface at 275°C, which corresponds to the optimal ALD process temperature, considerable arsenic oxide consumption was observed at the 1st TDMAH exposure. The arsenic oxide removal continued during subsequent ALD cycles albeit at a reduced rate. For similar experiments performed at 200°C, the arsenic oxide consumption was significantly lower than that at 275°C in agreement with the observations of Suri et al.[1] A clear ligand exchange process is identified through the alternate appearance of the CH and OH terminated surfaces. However, additional byproducts that contain -C=N- bonds are produced during the water pulse and accumulate in the film. Isotope exchange experiments indicate that these species are compatible with the formation of methylmethyleneimine (MMI) that may be produced through a beta hydride elimination pathway. [2,3]

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[2] C. M. Truong, P. J. Chen, J. S. Corneille, W. S. Oh, and D. W. Goodman, J. Phys. Chem. **99**, 8831 (1995).

[3] M. Bouman and F. Zaera, J. Electrochem. Soc. **158**, D524 (2011).

3:40pm TF+PS-MoA6 Precursor Design: Controlling Melting Point, Volatility, Reactivity and Other Important Characteristics of CVD and ALD Precursors, *Seán Barry,* Carleton University, Canada **INVITED**

Chemical vapour deposition methods (CVD) including atomic layer deposition (ALD) are relatively forgiving processes in many respects: the pressure does not have to be very low or strictly controlled, and to some extent the temperature of deposition likewise can have a certain amount of error. These forgiving conditions are largely due to the fact that growth of a film by CVD and ALD is controlled by the surface chemistry of the precursor used, as well as the behaviour of the precursor under thermal stress and in the gas phase. It is often said that precursor "design" is important in these fields: this refers to the control over several key characteristics of the precursor with respect to thermal and chemical behaviour.

My research hinges on the design of precursors with respect to four key characteristics, and each will be discussed using examples. Control of melting point is important to allow better kinetics of evaporation, and this can be tuned by ligand design and asymmetry in the precursor compound. Volatility is a key factor for a precursor, and this can be controlled many ways, including the coordinative saturation of the central (typically metal) atom of the precursor. Thermal stability and chemical reactivity are intimately related, and here choice of ligand, and knowledge of gas phase and surface chemistry is critical for fine control over the difference between a CVD precursor (which undergoes continual deposition) and an ALD precursor (which requires at least a measure of surface stability to allow for self-limiting behaviour).

4:20pm TF+PS-MoA8 Characterizing Vapor Delivery of μ^2-η^2-(^{t}Bu-Acetylene)Dicobalthexacarbonyl (CCTBA) for Deposition Processes, *James Maslar, W.A. Kimes, B.A. Sperling,* National Institute of Standards and Technology (NIST), *R. Kanjolia,* SAFC Hitech

Cobalt metal is a promising material for the formation of enhanced copper barrier and/or seed layers for copper interconnects in integrated circuits. For these applications, atomic layer deposition of cobalt using a gas-phase precursor can provide advantages in the device fabrication process. μ^2-η^2-(^{t}Bu-acetylene)dicobalthexacarbonyl (CCTBA) is a cobalt precursor that can be delivered as a vapor in a carrier gas. However, CCTBA exhibits a relatively low vapor pressure at ambient conditions and typically must be delivered at elevated temperatures to increase the amount of material delivered to the growth surface. As is typically the case for deposition precursors, prolonged heating can lead to decomposition of CCTBA. Therefore, this work was undertaken to help identify optimal delivery conditions for CCTBA by investigating 1) the decomposition of CCTBA in an ampoule at various ampoule temperatures and 2) the delivery of CCTBA from an ampoule as a function of carrier gas flow rate, system pressure, and ampoule temperature. CCTBA decomposition in an ampoule was investigated by using Fourier transform infrared (FT-IR) spectroscopy to identify the species present in the headspace of a CCTBA-containing ampoule as a function of time and ampoule temperature. CCTBA delivery was investigated using two optical techniques installed onto a delivery line from the ampoule. Optical access to the delivery line was achieved using two custom-built in-line optical flow cells that were designed to minimize perturbations to the gas flow. One flow cell was utilized for time-resolved FT-IR spectroscopy. This technique was used to identify the species entrained in the carrier gas. However, time response was limited to ~150 ms which is insufficient to resolve many thermal processes impacting CCTBA entrainment. In order to improve time resolution, a CCTBA-specific region of the mid-IR spectrum was identified and a direct optical absorption technique designed for CCTBA. This techinque employed a broadband infrared source with a mid-IR bandpass filter for isolating CCTBA-specific absorption features. This technique was installed on the second optical flow cell and used to measure the time-dependent CCTBA partial pressure as a function of gas flow rate, system pressure, and ampoule temperature for each CCTBA pulse with a time resolution of ~5 ms. In this manner, the dependence of CCTBA partial pressure on delivery conditions was identified. From these data and the time-dependent partial pressure data obtained with this optical measurement, the dependence of the actual amount of CCTBA delivered on delivery conditions was calculated.

4:40pm TF+PS-MoA9 Effect of Precursor on Coating Uniformity in Mesoporous Metal Oxide Films during Steady and Hold-Step ALD Processes, *Berç Kalanyan, M.D. Losego, G.N. Parsons,* North Carolina State University

Mesoporous film substrates with surface areas greater than 100 m^2/g see use in a variety of applications, most notably in photovoltaic and photoelectrochemical energy conversion. Pastes composed of 10-20 nm diameter metal oxide particles (ITO, FTO, ATO, TiO$_2$) are cast as a thick film and sintered to form conductive substrates. Atomic layer deposition (ALD) is uniquely suited to apply conformal coatings into these types of mesostructured films. To date, ALD coatings have been used in this fashion for dye sensitized solar cells, photoelectrochemical cells, and thermal photovoltaic devices. Beyond common "steady" or "continuous-flow" ALD processes, several research groups have explored the use of "gas hold steps", where the reactor is isolated from the pump for some period of time during the precursor exposure, for example, to enhance precursor infusion into high surface area or porous substrates.

In this study we examine ALD processing under steady and hold-step sequences for applying TiO$_2$ coatings into mesoporous Sn-doped indium oxide (ITO). Typical mesoposous films are up to 10 μm thick, which represents the minimum distance (without tortuosity) that precursor vapors need to travel in order to reach the bottom of the mesostructure. We choose two Ti-containing precursors, titanium tetrachloride (TiCl$_4$) and titanium tetraisoproproxide (TTIP), to understand the influence of bulky functional groups on precursor diffusion. The TTIP diffusivity will be smaller than TiCl$_4$, but it is also sterically hindered by its larger molecular size. We characterize film uniformity in mesoporous substrates by dynamic time-of-flight secondary ion mass spectrometry (TOF-SIMS), in-situ quartz crystal microbalance (QCM), and Krypton gas adsorption experiments.

We show that the TiCl$_4$/H$_2$O process can readily infiltrate into nanoporous ITO films as thick as 15 μm using a typical ALD process sequence, without gas "hold" steps. On the other hand, SIMS analysis shows that TiO$_2$ films deposited using TTIP and H$_2$O under the same exposure condition reach a depth of only 6 μm before exhibiting a large decay in TiO^{-} secondary ion intensity. While the TiCl$_4$ shows much better coverage, the process suffers from potential contamination, for example, from Cl which is observed in SIMS analysis. Therefore the use of bulky precursors such as TTIP is

critical for ALD infiltration into mesoporous substrates, especially under conditions where coating impurity content is an important concern.

5:00pm TF+PS-MoA10 Study of the Growth of Zinc Tin Oxide As Model System for Ternary Metal Oxide Atomic Layer Deposition, *Adriaan Mackus, R.W. Johnson, W.-H. Kim, S.F. Bent*, Stanford University

In recent years there is increasing interest in atomic layer deposition (ALD) processes that go beyond traditional AB cycles to enable the deposition of alloyed, doped, or ternary materials. The composition of a ternary material can be tuned by mixing the cycles of two different AB processes in a certain ratio $((AB)_n(CD)_m)$. However, in practice, the composition and the growth rate tend to deviate from what is expected based on the cycle ratio n/m, whereas the formation of a certain crystallographic phase strongly depends on the mixing of ALD cycles and post-deposition anneal conditions. A detailed understanding of how to deposit ternary metal oxides with control of composition and crystallographic phase is currently lacking.

In this work, the material zinc tin oxide (ZTO) has been selected as a model system for studying ternary metal oxide ALD, motivated by its applications as transparent conducting oxide (TCO)[1] or buffer layer[2] in solar cells. For these applications it is important that ZTO consists of earth-abundant non-toxic elements, and therefore has the potential to replace indium-based TCOs or Cd-based buffer layers. ZTO films were deposited by combining the ALD processes of ZnO from diethylzinc (DEZn) and water, and SnO_2 from tetrakis(dimethylamido)tin (TDMASn) and water.[1,3] Synchrotron-radiation X-ray diffraction (SR-XRD) has been performed at the Stanford Synchrotron Radiation Lightsource (SSRL) to investigate the crystallographic phase of the films as a function of composition, cycle ratio, and anneal conditions. It was found that the zinc orthostannate (Zn_2SnO_4) phase forms upon high-temperature annealing, thereby confirming the deposition of ZTO. In addition, Fourier transform infrared spectroscopy (FTIR) was employed to elucidate the surface chemistry of the ZTO ALD process.

1. Mullings *et al.*, Thin Solid Films **556**, 186 (2014)

2. Lindahl *et al.*, Prog. Photovolt: Res. Appl. **21**, 1588 (2013)

3. Mullings *et al.*, J. Vac. Sci. Technol. A **31**, 061503 (2013)

2D Materials Focus Topic
Room: 310 - Session 2D+AS+BI+PS+SS-TuM

2D Materials: Surface Chemistry, Functionalization, Bio and Sensor Applications
Moderator: Richard Osgood, Columbia University

8:00am 2D+AS+BI+PS+SS-TuM1 Phase Engineering in 2D Transition Metal Dichalcogenides, *Manish Chhowalla*, Rutgers University **INVITED**
Two-dimensional transition metal dichalcogenides (2D TMDs) — whose generalized formula is MX_2, where M is a transition metal of groups 4–7 and X is a chalcogen — exhibit versatile chemistry and consist of a family of over 40 compounds that range from complex metals to semiconductors to insulator. Complex metal TMDs assume the 1T phase where the transition metal atom coordination is octahedral. The 2H phase is stable in semiconducting TMDs where the coordination of metal atoms is trigonal prismatic. Unlike mechanical exfoliation and chemical vapor deposition, chemical exfoliation of semiconducting layered TMDs yields monolayered nanosheets with heterogeneous atomic structure consisting of metallic (1T) and semiconducting (2H) phases. Metal (1T phase) to semiconductor (2H phase) transition can be achieved via mild annealing of exfoliated materials. Semiconductor to metal transitions can be achieved via chemistry. The 1T phase in *semiconducting* TMDs has scarcely been studied but it deserves urgent attention as it exhibits promise as a hydrogen evolution catalyst and as contact electrode in electronic devices. We will describe these phase transitions in semiconducting TMDs and provide examples of how we have learned to exploit them for covalent functionalization, enhanced catalytic and electronic performance.

8:40am 2D+AS+BI+PS+SS-TuM3 Transition Metal Nanoparticles on Single-Layer MoS₂: Structural, Electronic and Catalytic Properties, *Takat B. Rawal*, D.T. Le, T.S. Rahman, University of Central Florida
We will present results of density functional theory based calculations of the geometric and electronic structure of several types of sub-nanometer sized transition metal nanoparticles (TMNPs) on pristine and defect-laden single-layer MoS_2. We will show that among the investigated TMNPs (Cu, Ag, Au), Cu nanoparticles bind strongest to pristine MoS_2 while Au and Ag nanoparticles bind with similar, weaker strengths. The presence of the vacancy defect on MoS_2 enhances significantly the binding strength of Cu nanoparticles, while it has very little effect on the binding strength of Au NPs. More interestingly, the amounts of charge transfer from TMNPs to MoS_2 vary following the order of the bind energies of TMNPs on MoS_2. Additionally, the shape of the nanoparticles also has an impact on the binding characteristics. Of particular interest is the role of the substrate on the catalytic properties of the TMNP and conversely that of the TMNP on the defect-laden MoS_2 single layer. In this regard we will examine in detail the reactivity of the atoms at the TMNP/MoS_2 interface in reactions such as CO oxidation and methanol decomposition and compare them to that of similar nanoparticles when supported on titania.

Work supported in part by DOE Grant No. DE-FG02-07ER15842

9:00am 2D+AS+BI+PS+SS-TuM4 How Fluorination Enhances Friction Forces for Graphene, *Xin Liu*, Q. Li, University of Pennsylvania, S.P. Kim, Brown University, V.B. Shenoy, University of Pennsylvania, P.E. Sheehan, J. Robinson, Naval Research Laboratory, R.W. Carpick, University of Pennsylvania
The chemical functionalization of graphene can alter its electronic, chemical, mechanical, and tribological properties. Here we employ atomic force microscopy (AFM), Raman microscopy, and molecular dynamics (MD) simulations to show that friction can be fine-tuned by chemically modifying graphene. Although bulk fluorinated graphite has a very low surface energy, our experiments and simulations both show that friction between nanoscale tips and FG is up to 9 times higher than that for pristine graphene. The ability to resolve an ordered lattice in atomic stick-slip friction measurements also diminishes with greater fluorination, indicating that the fluorinated graphene is disordered. Our observation suggests that AFM friction measurements provide a sensitive local probe of the degree of fluorination of graphene. Motivated by MD simulations, we propose that the dramatic enhancement of friction results from increased corrugation of the interfacial potential due to the strong local charge concentrated at fluorine sites, consistent with the Prandtl-Tomlinson model.

9:20am 2D+AS+BI+PS+SS-TuM5 Chemical, Structural and Electrical Modification of Graphene, *Sandra Hernández*, E.H. Lock, M. osofsky, S. Tsoi, Naval Research Laboratory, C. Junkermeier, Penn State University, R. Stine, Nova Research, J. Robinson, Naval Research Laboratory, A. Nath, George Mason University, V.D. Wheeler, R.L. Myers-Ward, J. Caldwell, C.R. Tamanaha, T. Reinecke, P.E. Sheehan, D.K. Gaskill, S.G. Walton, Naval Research Laboratory
2D nanomaterials have been vigorously investigated due to their superlative mechanical, thermal, and electronic properties. Being composed entirely of surface atoms, they are incredibly amenable to surface modification thus providing the opportunity towards excellent control over their properties. Surface engineering of 2D materials composed of carbon materials, such as graphene, can be achieved by plasma modification. We will discuss our efforts in understanding the chemical, structural, and electrical properties of plasma functionalized graphene by introducing -oxygen, -fluorine, and -nitrogen chemical moities, and discuss their impact on chemical reactivity, electrical transport, and enhanced sensing behavior. Demonstrating how precise nano-engineering of surface chemistry impacts contact engineering, biosensing and device based applications.

This work is supported by the Naval Research Laboratory Base Program.

9:40am 2D+AS+BI+PS+SS-TuM6 The Mechanochemistry of Chemically Modified Graphene, *Jonathan Felts*, S.C. Hernandez, A.J. Oyer, J. Robinson, S.G. Walton, P.E. Sheehan, Naval Research Laboratory
Defining the optoelectronic properties of graphene through controlled chemical functionalization provides a route to fabricating a wide range of graphene based devices. In prior work, we showed that heat supplied by a scanning probe removed functional groups from chemically modified graphene (CMG) thereby restoring it to graphene [1]. Here we show that mechanical stress alone effectively removes functional groups. We measured the degree of surface functionalization by monitoring both normal load and friction between the sliding tip and a plasma processed CMG sheet. For oxygenated graphene, friction decayed exponentially with sliding distance, dropping to ~15% of the starting value. These measurements revealed an initial drop in friction that was independent of applied stress, suggesting the presence of an adsorbed water layer on the surface. More importantly, they reveal an Arrhenius-like relationship between contact stress and degree of surface reduction. The reduction in friction persisted, precluding the presence of the adsorbed contaminants as the source of the friction change. Conductive AFM and Raman measurements provide further evidence for chemical reduction. Conductive diamond AFM tips measure the current through the surface during the reduction process, revealing a 5x increase in conductivity corresponding to the friction force reduction. Additionally, Raman measurements on a 5 mm² reduced area showed a relative increase in both the G and 2D peaks, consistent with a reduction in functionalization. These experiments enabled detailed comparison of tribochemical reactions without the complications of transfer films or the initial run-in of the film. They also enable experiments difficult by other means. For instance we could directly compare the mechanical barrier to functional group removal by monitoring friction while slowly ramping the applied stress between the tip and a graphene surface functionalized with either oxygen or fluorine groups. For oxygenated graphene, the contact stress at the maximum reduction rate was ~0.47 ± 0.14 GPa; for fluorinated graphene it was ~0.85 ± 0.27 GPa. Thus, by using the same tip and same supporting substrate we could directly compare the bond strengths between different functional groups and the graphene lattice. This work demonstrates the ability to measure and control the chemistry of single-layer functionalized surfaces at the nanometer scale, and has wide application in tribochemical wear, mechanochemistry, and nanoelectronic device fabrication with chemically tuned optoelectronic properties.

[1] Z. Wei, et al, *Science* **328**, 1373-1376 (2010)

11:00am 2D+AS+BI+PS+SS-TuM10 Fe-catalyzed Etching of Graphene, Few-Layer Graphene, and Graphite, *Guangjun Cheng*, A.R. Hight Walker, National Institute of Standards and Technology
Mechanically exfoliating graphite onto a substrate provides a family of layered materials with adjustable thickness, including monolayer graphene, few-layer graphene (FLG), and graphite. In this work, we investigated the Fe-catalyzed etching of graphene, FLG, and graphite in forming gas (10% H_2/90% N_2) or N_2 using low-voltage scanning electron microscopy and Raman spectroscopy. Fe thin films were deposited by sputtering onto mechanically exfoliated graphene, FLG, and graphite flakes on a Si/SiO₂ substrate. When the sample is rapidly annealed in either gas environment, particles are produced due to the dewetting of the Fe thin film and expected to catalyze the etching of graphene, FLG, and graphite. The combined microscopic and spectroscopic evidence reveals a thickness-dependent,

catalytic etching behavior in these two gas environments and provides insights into the catalytic mechanisms involving carbon hydrogenation and carbon dissolution.

11:20am 2D+AS+BI+PS+SS-TuM11 Tunable Graphene/Si Schottky Diode Sensor: Before and After Functionalization for Wide Range of Molecular Sensing, *MdAhsan Uddin*, A. Singh, T. Sudarshan, M.V.S. Chandrashekhar, G. Koley, University of South Carolina

Graphene/Semiconductor Schottky devices attracted significant research attention due to wide range of applications from transistor to IR detector [1-2]. Such heterojunctions are also promising for sensing applications due to the molecular adsorption induced Schottky barrier height (SBH) change at the interface, affecting the junction current exponentially in reverse bias, which leads to ultrahigh sensitivity. Graphene/p-Si diode sensor [Device image, Raman spectra and I-V characteristics shown in fig. 1(a), (b) and (c)] has been developed with high bias-dependent sensitivity and low operating power.

Performance enhancement has been demonstrated by fabricating graphene chemiresistor and diode sensor on the same chip. The diode sensor exhibited 13 times higher sensitivity for NO_2 [Fig. 2(a)] and 3 times higher for NH_3 [Fig. 2(b)] in ambient condition, while consuming ~500 times less power for same applied voltage. Sensing tunability is achieved by operating the device in reverse bias, tuning the graphene work function and hence the SBH by the applied bias. The sensitivity varied from 268 to 574% for NO_2 as the bias magnitude varied from -1 to -8V [Fig. 3(a)]. Optimized sensor design to detect particular analyte is also possible by careful selection of graphene/Si heterojunction SBH. For example, graphene/p-Si with larger SBH is better NO_2 sensor while smaller SBH device has better NH_3 sensitivity. The sensing mechanism based on SBH change has been confirmed by capacitance-voltage measurements [Fig. 3(b)]. The SBH decreased by 0.23eV for NO_2 exposure while increased by 0.16eV for NH_3. Variation in sensitivity with NO_2 and NH_3 concentration has also been demonstrated (Fig. 4).

Pd and Pt functionalization has been carried out to make the graphene/Si diode [Fig 5] sensitive to H_2. Extrapolated SBH from the I-V characteristics, before and after few nm metal decoration, and H_2 exposure showed initial SBH decrease after functionalization and subsequent increase in presence of H_2, respectively [Fig. 6(a) and (b)]. Compared to graphene chemiresistor, the chemi-diode sensor offers more than one order of magnitude higher H_2 sensitivity for both types of functionalization. Similarly, the reverse bias operation also enables low power consumption, tunable sensitivity and detection of H_2 down to 1 ppm [Fig. 7(a)] in air which is close to the atmospheric background of 0.6 ppm [3]. Among the two metals, Pd-functionalization always exhibited better sensing response irrespective of the bias voltage [Fig. 7(b)]. Remarkably, for Pd-functionalization, the sensor response showed absolute exponential change with varying H_2 concentration ranging from 2 to 1000 ppm [Fig. 7(c)].

12:00pm 2D+AS+BI+PS+SS-TuM13 Dielectrics Layer Deposition on Graphene Surface by Functionalization with Polar Titanyl Phthalocyanine, *Jun Hong Park*, I.J. Kwak, K. Sardashti, A.C. Kummel, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulators on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPc) on 2D semiconductors directly as a monolayer low-k dielectric or as a nucleation layer for growth of high-k insulators. This study demonstrates the molecular scale observation of formation of O-TiPc mono and bilayers on graphene with UHV scanning tunneling microscopy (STM). O-TiPc monolayers were deposited on HOPG surfaces by organic molecular beam epitaxy. After deposition, O-TiPc forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.4 x 1.4 nm grid. Observation of bright protrusions on each O-TiPc indicates that each O-TiPc in the monolayer is directed outward to vacuum. STS shows the band gap of the monolayer is 1.7 eV and the band gap of the bilayer is 2.3 eV. The monolayer or bilayer can directly be employed for sub-nanometer insulators on 2D semiconductors at low bias. Multiple cycles of TMA and water were dosed onto O-TiPc/HOPG to investigate nucleation of Al_2O_3 on the O-TiPc layers. The first cycle of TMA was observed to chemisorb on a 1.4 x 1.4 nm grid on the TiOPc monolayer. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H_2O), insulating aluminum oxide was deposited uniformly on O-TiPc/HOPG. After formation of Al_2O_3 on O-TiPc/HOPG, the band gap of surface increases from 1.7 eV to 2.7 eV, while the conductance decreased. As shown in XPS spectra, the quality of Al_2O_3 can be improved by post annealing, consisting with transition of chemical states in O 1s peak and Al

2p. The chemical shifts of O and Al indicate that post annealing converts remained the Al-OH to Al_2O_3. Consequently, O-TiPc can not only act as a low-K dielectric but also induce high density ordered nucleation of ALD on central ion of O-TiPc for high-k dielectric growth.

Plasma Science and Technology
Room: 308 - Session PS-TuM

Plasma Surface Interactions I
Moderator: Jane P. Chang, University of California at Los Angeles

8:00am PS-TuM1 Directed Irradiation Synthesis: Manipulating Matter in Nanoscale Self-Organized Systems, *Jean Paul Allain*, Z. Koyn, B. Holybee, S. Arias, University of Illinois at Urbana-Champaign **INVITED**
Deciphering self-organization mechanisms of nanostructures (e.g. nanodots, ripples) on compound semiconductors and silicon via low-energy ion-beam assisted plasma irradiation is critical to manipulate functionality in nanostructured systems. By operating at ultra-low energies near the damage threshold, irradiation-driven defect engineering can be optimized (e.g. 10-500 eV). Tunability of optical, electronic, magnetic and nuclear detection properties is realized by reaching metastable phases controlled by irradiation. This talk summarizes emerging research that exploits irradiation-driven materials modification with applications in: nanophotonics, nanoelectronics, biomaterials and nuclear detection. Furthermore advances of in-situ analysis conducted during modification to correlate tunable irradiation synthesis and device performance will be summarized.

8:40am PS-TuM3 Contact Resistance Degradation Caused By Plasma Charging of Silicon on Insulator During Contact Etch, *Todd Bauer*, J.F. DiGregorio, R.L. Jarecki Jr., Sandia National Laboratories
Contact formation is of enduring importance to integrated circuit manufacturing. A typical contact etch process uses fluorocarbon plasmas to etch small diameter, high aspect ratio holes through deposited silicon dioxide, landing on silicide. Contact etch processes provide high etch rate selectivity due to fluorocarbon polymer deposition on non-oxide surfaces. This selectivity is necessary for bi-level contacts landed on gates and active Si but the interactions among etching, deposition, and the structures being formed are complex and given to non-obvious failure modes. In this presentation we report on the characterization of a failure mode in which contacts to device Si on silicon-on-insulator (SOI) wafers form voids between the interconnect plug and the underlying silicide after thermal stress. The initial parametric signature was an increase in contact resistance for Kelvin structures of a specific design. From a nominal resistance of 2.5Ω, resistance increases by a factor of 3 were common. Through destructive physical analysis we correlated the increase in Kelvin resistance to the formation of small voids at the base of the Kelvin contact. We developed the following model to describe the condition that leads to the voids. As the contact etch reaches the Si surface, the potential at the bottom of the hole shifts abruptly from equilibrium, balancing electron and ion currents, to a more positive potential. This positive potential suppresses ion bombardment at the base of the contact, reducing etch rate and allowing more fluorocarbon polymer to accumulate. Electron current to the bottom of the hole increases to equilibrate the disturbed potential, but is limited by electron shadowing and the available contact hole area. The duration of the excess positive potential is proportional to the specific capacitance of the revealed Si surface, which, for islands on SOI wafers with shallow trench isolation, may be thousands of times larger than an equivalent bulk wafer. Smaller contact area (i.e. fewer contact holes) in a single island exacerbates the transient potential duration and the resulting etch process disturbance. We developed test structures and executed experiments to explore the transient potential concept and the local Si capacitance relative to the open contact area. Without adequate mitigation, the accumled polymer leads to a weakened interconnect interface that is vulnerable to voiding and delamination.

Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a Lockheed Martin Corporation, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:00am PS-TuM4 3D Modeling of SiN Etching by Hydrofluorocarbon Plasma, *Nobuyuki Kuboi*, T. Tatsumi, T. Kinoshita, T. Shigetoshi, M. Fukasawa, J. Komachi, H. Ansai, Sony Corporation, Japan
Silicon nitride (SiN) is as essential as silicon (Si) and silicon oxide (SiO_2) for fabricating complementary metal oxide semiconductor (CMOS) devices.

Damage on Si substrates is caused during etching of the transistor side-wall and the contact through the drain region [1], and this can greatly affect transistor properties. Hence, for CMOS devices to achieve high performance, it is important to control the etching process quantitatively along with the mechanism of the SiN surface reaction.

We propose a surface reaction model for the SiN etching process by fluorocarbon ($C_4F_8/O_2/Ar$) and hydrofluorocarbon ($CH_2F_2/O_2/Ar$) plasma based on the Slab model of SiO_2 [2]. The surface layer is assumed to consist of two layers: a reactive layer divided by several thin slabs and a deposited C-F polymer layer on the reactive layer. We considered physical and chemical reactions in detail including reactivity of radicals (C, F, O, and H), dangling bonds ratio, outflux of N, and generation of by-products (HCN, C_2N_2, CH, CF_2, SiF_2, and SiF_4) as ion assist, which depend on process parameters. We confirmed that absolute values and trends of SiN etch rate, polymer thickness, damage thickness, and selectivity of SiN/SiO_2 and SiN/Si along with gas flow rates of C_4F_8 and CH_2F_2 were consistent with experimental data of conductively coupled plasma.

Furthermore, to analyze 3D damage distribution affected by the etched profile, we developed a new 3D simulation technique using an extended voxel model (called "smart voxel") also including the above Slab model. By using gas fluxes with local pattern effect, the Slab model is solved at each voxel. Then, the etch rate and thicknesses of polymer and damage are derived. Smart voxel has details of the history of the etching situation and gives them around existing voxels when etch front is evolved in the next calculation time step. By repeating these procedures, 3D damage distribution considering a time-dependent etched profile can be realized. In addition to this new concept, modeling of gas transportation in the pattern treated as fluid is adopted without interaction between voxels, which is different from a Monte Carlo (MC) method. Hereby, 3D damage for multi-layer ($Si/SiN/SiO_2$) can be predicted much faster and more accurately than the conventional MC model in spite of a large scale micro-meter. We will show a 3D etched profile and damage distribution for SiN side-wall etching and discuss how to control etching parameters to achieve low damage.

Acknowledgements: We thank Prof. S. Hamaguchi for stimulating discussion.

[1] K. Katahira *et al*. J. Vac Sci. Technol. *A27*, (2009) 844.

[2] N. Kuboi *et al*. Jpn. J. Appl. *50*, (2011) 116501.

9:20am **PS-TuM5 Study of Plasma-Surface Interaction in HBr/Cl₂/O₂ ICP**, *Ashutosh Srivastava*, University of Houston*, T. Ohashi,* Hitachi High-Technologies*, V.M. Donnelly*, University of Houston

HBr plasmas are used to etch Si, as well as GaN, PZT, InP, Indium Zinc Oxide and other materials. In Si etching, HBr plasmas create better anisotropic profiles than Cl_2 plasmas, with better selectivity toward SiO_2. Selectivity can be further improved by adding oxygen to the plasma. The feed gas composition of $HBr/Cl_2/O_2$ plasmas is optimized to best meet the needs of the particular application. Keeping such a complex process stable over time requires tight control over all plasma parameters, including reactor wall conditions. Here, we have studied the interaction of $HBr/Cl_2/O_2$ inductively-coupled plasmas (ICP) with the etching products-coated reactor walls, using the "Spinning Wall" technique. Surface composition was determined by Auger electron spectroscopy, and species desorbing from the surface were detected by quadrupole mass spectrometry. It was observed that in a pure HBr ICP with no Si etching, an oxygen plasma-conditioned surface SiO_x layer remained unaltered, indicating the inability of Br-containing species to break the Si-O bond. When 5-50% oxygen was added to HBr ICPs, large fluxes of H_2O were found to desorb from the spinning wall surface, peaking at ~20% O_2. The H_2O signal dependence on spinning wall rotation frequency indicates that the reaction time, and/or water retention time on the surface is of the order of 10's of ms. After turning off the plasma, signal could be detected for several minutes. This is likely because of the highly disorder surface, leading to a stretched exponential decay of water desorption. Addition of Cl_2 to an HBr ICP (1:1 ratio) resulted in small amount (<3%) of Cl on the surface but no Br. This Cl was not removed by a pure HBr ICP, but was in an O_2 ICP. When a self-bias of -120Vdc was applied to the Si substrate in an HBr ICP, a Si:O:Br layer (32:7:60) was deposited on the spinning wall surface. As O_2 was added, the surface composition changed from a Br-rich layer at 6% O_2 to an O-rich layer at 20% O_2. Si etching in a Cl:HBr ICP (1:1) resulted in equal amounts of Cl and Br on the surface. Again, when O_2 is added the surface transitions from Cl-rich at 6% O_2 to Cl/O-rich at 20% O_2 and finally to O-rich at 40% O_2.

9:40am **PS-TuM6 Experimental Evaluation of Ta Film Etching Characteristics by CO⁺ Ion Irradiation**, *Makoto Satake*, Hitachi, Japan*, H. Li, K. Karahashi, S. Hamaguchi*, Osaka University, Japan

Magnetic Random Access Memory (MRAM) is considered as a promising candidate for the next generation memory because of its non-volatility, fast reading or writing speed, and high write-cycle endurance. MRAM consists of magnetic tunnel junctions (MTJ) and CMOS devices. One of the issues concerning MRAM fabrication is the development of a nano-scale anisotropic etching technology for MTJ because an MTJ is used as the memory component of an MRAM device and high integration of MTJs is required for commercially competitive MRAM chips. One approach to MTJ etching is to use CO/NH₃ plasmas with Ta hard masks. With this process, vertical etching profiles with a taper angle of 80° have been achieved with high etching selectivity of magnetic materials over Ta [1].

In previous research [2], etching yields of Ta and Ni films were evaluated with a mass-selected ion beam system with incident ions of Ar^+, N^+, O^+, and CO^+. It has been found from X-ray photoelectron spectroscopy (XPS), for example, that the Ta film surface was oxidized while the Ni film surface was not oxidized by the same CO^+ ion irradiation. Therefore, it was concluded that the oxidized layer of Ta, which was formed by CO^+ irradiation, suppressed the Ta etching yield.

In this study, Ta etching yields by CO^+ ions were compared with corresponding theoretical values of physical sputtering of Ta to understand why the Ta etching yield by CO^+ ion irradiation was typically very low. The experimentally obtained sputtering yield is typically about 1 % of the theoretical yield of physical sputtering by non-reactive incident species of the same mass. Our XPS analysis of Ta after CO^+ ion irradiation indicates that the Ta film is highly oxidized (i.e., to the equivalent degree of Ta_2O_5) by CO^+ ion irradiation while Ar^+ ion irradiation of a Ta oxide film reduces its oxidation degree. Therefore the low Ta etching yield by CO^+ ion irradiation is caused by a larger amount of oxygen supply by incident CO^+ ions with less oxygen sputtering. The dependence of the Ta sputtering yield by CO^+ ions on the ion incident angle will be also discussed in terms of the angle dependence of the surface oxidation level.

[1] N. Matsui, et al., *Vacuum* **66**, 479-485 (2002).

[2] H. Li, et al., *AVS* **60**[th] *Int. Symp* (2013).

11:00am **PS-TuM10 Study of Hydrofluorocarbon Precursor Parameters for Plasma Etching of ULK Dielectric**, *Chen Li*, *G.S. Oehrlein,* University of Maryland, College Park*, R. Gupta, V. Pallem*, Air Liquide

Plasma etching of ultra-low k (ULK) dielectrics requires gas precursors that enable very high etching selectivity of ULK over the mask and underlayer while minimizing ULK sidewall damage. We report a systematic study aimed at evaluating the impact of the nature of hydrofluorocarbon gas precursors on plasma etching performance of a representative ULK material, Black Diamond II (BDII) coated onto Si. The work was performed in a dual frequency capacitively coupled plasma (CCP) reactor with real-time characterization by ellipsometry, optical emission spectroscopy (OES), and electrical measurements. The chemical composition of deposited films and post plasma low-k surfaces was examined by X-ray photoelectron spectroscopy (XPS). Etching selectivity of BDII over amorphous carbon (aC), SiO_2 and Si_3N_4 masking materials was evaluated. The impact on the ULK material when exposed under sidewall-like plasma conditions was also studied for various precursor gases using the dilute HF etching method. The precursor gases studied included fluorocarbon (FC) and hydrofluorocarbon (HFC) precursors whose molecular weights and chemical structures were systematically varied i.e. fluorine/carbon ratio, presence/absence of carbon double bonds, and ring versus linear structure. The plasma process conditions were Ar with FC (or HFC) and O_2 admixture at a fixed total pressure with varying ion energies. The etch rate (ER) and deposition rate (DR) were measured by *in-situ* ellipsometry. We found that the DR was greater for precursors with a larger degree of unsaturation. Linearly shaped gases with higher F/C ratio showed the best etching performance, evaluated by the maximum value of product of BDII ER and BDII/aC selectivity value for each gas. By relating measured CF_2 optical emission for varying precursor concentrations to simultaneously determined FC (or HFC) film DR, we distinguished three deposition behaviors with qualitatively different etching performance based on the precursor structure. A gap structure, blocking direct ion bombardment, was used to simulate the sidewall plasma environment. With this approach, the evolution of the physical and chemical sidewall profile can be studied in real time using *in-situ* measurements. We found that gases exhibiting a particular deposition behavior differed systematically in formation/absence of a protective fluorocarbon film on the ULK sidewall. The dependence of improvements in low-k etching performance on the FC chemical structures and the surface model for underlying mechanisms relating these properties will be reported.

11:20am **PS-TuM11 Characteristics of Reactive Ion Etching Processes for ITO and ZnO**, *Hu Li*, *K. Karahashi*, Osaka University, Japan*, M. Fukasawa, K. Nagahata, T. Tatsumi*, Sony Corporation, Japan*, S. Hamaguchi*, Osaka University, Japan

With the increasing demand for high-resolution optoelectronic devices and their applications, micro-pattern formation of transparent conducting oxides (TCOs), especially that of tin-doped indium oxide (ITO), has been required

more frequently than before in the development of such devices. Since ITO contains indium, which is one of minor metals whose global production is typically small and are generally traded at high prices, less expensive alternative materials for TCOs are highly sought after. Zinc oxide (ZnO) is a possible candidate for such TCOs alternative to ITO.

Micro-pattern formation of thin film materials may be achieved by reactive ion etching (RIE), which uses chemically reactive plasmas that typically allow high selectivity of etching of specific materials over others and high controllability of micro/nano-scale structure formation. RIE has been widely used in fabrication processes of semiconductors. For high-resolution optoelectronic devices, there has been a considerable demand for RIE processes of ZnO with CH_4 based plasmas, which is a non-corrosive gas and expected to yield high etching rates for ZnO. The RIE process of ZnO with CH_4 based plasmas, however, has also various problems such as carbon deposition during the etching processes. To further develop RIE technologies of ZnO by CH_4 based plasmas, a better understanding of elemental processes of plasma-surface interactions of CH_4 based plasmas with ZnO.

In this study, sputtering yields and surface reaction characteristics of ITO and ZnO by energetic chemically reactive CH_x ions (CH^+ and CH_3^+) as well as inert-gas ions (Ar^+, Ne^+ and He^+ ions) were examined with the use of a mass-selected ion beam system. It has been found that, for physical sputtering, sputtering yields of ZnO are much higher than those of ITO. For ZnO, etching by CH_3^+ proceeds faster than Ar^+ physical sputtering, which indicates that the etching rate is enhanced by chemical interactions of CH_x^+ with ZnO. The chemical effect is more pronounced at a lower incident energy. With a fewer hydrogen atoms in the incident ion (i.e., in the case of CH^+ ion incidence), however, carbon deposition tends to take place on the ZnO surface. Similar beam-surface interactions of ITO with CH_x ions as well as inert-gas ions were also examined and compared with those of ZnO. Mechanisms of chemical reactions of CH_x ions with ZnO and ITO will be discussed in the presentation.

11:40am PS-TuM12 Selective Etch and Functionalization of Coblock Polymers, *Evgeniya Lock*, *S.G. Walton*, Naval Research Laboratory
Coblock polymers have been applied as nanotemplates for production of nanocomposites and biomolecules nanoarrays due to their ability to spontaneously form dense periodic spherical, cylindrical, and lamellar domains. The final nanostructure is typically produced after chemical etch or dry plasma-based etch in fluorine containing gas environment. However, systematic studies of the effects of plasma etching of coblock polymers in different gas environments are limited. Furthermore, selective chemical functionalization of one of the blocks, while the other one is etched will enable more robust biomolecules/nanoparticles integration and is of critical importance. In order to achieve nanoscale high resolution etch, a precise control of the plasma/surface interactions is needed.

We have already shown that electron beam-generated plasmas can introduce large range of chemical functionalities in a polymer surfaces and etch polymers with low etch rates [1, 2]. In this work, we will show the ability of these plasmas to achieve nanoscale etch of PS-b-PMMA in different gas environments. In addition, the effect of ion energy (1 to 100 eV) on features definition and etch depth will be evaluated. This work was supported by the Naval Research Laboratory Base Program.

References:

1. E. H. Lock, D. Y. Petrovykh, P. Mack, T. Carney, R. G. White, S. G. Walton and R. F. Fernsler, "Surface composition, chemistry and structure of polystyrene modified by electron-beam-generated plasma", *Langmuir,* 26 (11), 8857 (2010).

2. E. H. Lock, S. G. Walton and R. F. Fernsler, "Physio-chemical modifications of polystyrene and polypropylene surfaces by electron beam-generated plasmas produced in argon", *Plasma Process. Polym.* 6 (4), 234 (2009).

12:00pm PS-TuM13 Dry Etch Process Development for PMMA Removal Selectively to PS for sub-10nm Patterning, *Aurelien Sarrazin*, *P. Pimenta-Barros, N. Posseme, S. Barnola, A. Gharbi, R. Tiron*, CEA, LETI, MINATEC Campus, France, *C. Cardinaud*, CNRS-IMN, France
For sub-10nm patterns, the semiconductor industry is facing the limits of conventional lithography to achieve narrow dimensions. Presently, extreme ultraviolet lithography (EUV) is under development but this technology is not mature. On another hand, multiple patterning, which benefits from a tremendous technological knowledge in conventional lithography, deposition and etching processes, could be an alternative technique but its major drawback is the complexity of integration generating wafer cost increases. These issues encourage the development of limitless resolution and low cost techniques such as Directed Self Assembly (DSA). Indeed, DSA is one of the promising solutions to reach sub-10nm patterns with a high selectivity.

One challenge of DSA integration is the PMMA removal selectively to PS. Using dry etch for this step is mandatory for line application since wet cleaning is prohibited with the risk of pattern collapse. In this work we propose to study PMMA block plasma etching with a high selectivity over PS using oxidizing and reducing chemistries. All experiments have been carried out in a CCP etching chamber.

First a screening of these chemistries has been performed on PS and PMMA films showing that CO based chemistry is the most interesting process providing infinite selectivity to PS. To achieve this result, studies have been performed with different gases to evaluate the evolution of etch rate with the process time. Complementary analyses using X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) will also be presented for understanding volume and surface etch mechanisms.

These blanket results will be tested on lamellar block copolymers. The compatibility of these chemistries will be validated in term of etch rate, CD control using Scanning Electron Microscopy (SEM) and roughness using Atomic Force Microscopy (AFM). We will demonstrate that a trade-off is needed between high selectivity to PS and high etch rate to remove the PMMA.

Thin Film
Room: 307 - Session TF+PS-TuM

ALD for Emerging Applications
Moderator: James Fitz-Gerald, University of Virginia

8:00am TF+PS-TuM1 Atomic Layer Deposition: A New Strategy to Improve Metal Corrosion Resistance?, *Lorenzo Fedrizzi*, *E. Marin, A. Lanzutti*, University of Udine, Italy **INVITED**
Interests on nanometric conformal coatings are nowadays growing in a wide range of applications, from electronic components to corrosion protection, chemical barriers or even wear resistance. Atomic Layer Deposition (ALD) is one of the most promising nanometric deposition technologies which offers the possibility to obtain conformal coatings even on very complex tridimensional substrates of different chemical nature, with a strict thickness tolerance and strong adhesion. During an ALD cycle, only one molecular layer is deposited on the substrate surface, enabling the theoretical possibility to tailor the composition of the deposit up to molecular resolution, thus obtaining almost unique properties.

Therefore this technology appears to be an interesting and innovative alternative to the existing ones aimed to metal corrosion protection, such as electrodeposition, painting or other chemical or physical vapor deposition technologies.

This work describes the use of ALD for the corrosion protection of different metal alloys of common industrial interest such as stainless steels, aluminum or magnesium alloys. Moreover, the possibility of combining this deposition technology with some traditional ones is also discussed to the aim of obtaining improved protection properties by multilayer coatings able to enhance a protective barrier action.

8:40am TF+PS-TuM3 Atomic Layer Deposition of Thin VO_2 Films for Thermal Management Applications, *Virginia Wheeler*, *M. Tadjer, N. Nepal, M. Currie, Z.R. Robinson, M.A. Mastro, K. Cheung, F. Kub, C.R. Eddy*, Naval Research Laboratory
Vanadium oxides are thermochromic materials which have significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties due to a metal-insulator phase transition (MIT). These materials offer great advantages in a variety of applications including electrochemical applications, energy storage, thermoelectric devices, Mott transistors, and smart windows. In this work, atomic layer deposition (ALD) was used to produce thin, highly uniform, amorphous VO_2 films which enabled the ability to investigate the impact structure (amorphous vs. crystalline) has on the rate of change of intrinsic properties due to the MIT.

Amorphous VO_x films (5-45nm) were deposited by ALD at 150°C using tetrakis(ethylmethyl)amido vanadium and ozone precursors. X-ray photoelectron spectroscopy (XPS) was used to verify the quality, stoichiometry, and depth uniformity of the films. All as-grown films exhibited carbon surface contamination due to atmospheric transfer from the ALD to XPS chambers. Moreover, the top ~1nm of the film exhibited $V2p$ peaks at 517.7 and 516.3eV correlating to V_2O_5 and VO_2 components, respectively. At depths >1nm, XPS showed no residual carbon contamination and only a single VO_2 peak with a FWHM from 2-2.7 eV, which is similar to crystalline films and indicative of the high uniformity and quality of these films. XPS depth profiles near the VO_x/Si interface had

a low binding energy shoulder at 513.5 eV, suggesting that initially the films are very oxygen deficient.

The influence of *ex situ* anneal temperature (200-550°C), time (0.17-2hr), and gas environment (forming gas, Ar, O_2, and ozone) on the ability to obtain single phase, crystalline VO_2 films was also examined. Initial results show that only O_2 anneals produce crystalline VO_2, but other factors such as gas flow, duration, and temperature require optimization to inhibit multiphase, polycrystalline films.

Electrical and optical performance of amorphous and crystalline ALD films was assessed from 77-500K and 300-380K, respectively. Unlike crystalline VO_2 films that exhibit an abrupt, up to five orders of magnitude change in resistance around the MIT at 60°C (333K), amorphous VO_2 films had an exponential change in resistance of ten orders of magnitude over the entire temperature range studied. Also, an average activation energy of -0.20eV and temperature coefficient of resistance of 2.39% at 310K was extracted. These results suggest that amorphous VO_2 films, with less structural order, have the potential to induce larger, more gradual electrical changes that could be useful for bolometers or passive thermal management on spacecraft.

9:00am **TF+PS-TuM4 Atomic Layer Deposition of $Pb(Zr_XTi_{1-X})O_3$ Thin Films to Engineer Nanoscale Multiferroic Composites**, *Diana Chien*, *T. Kim, J.P. Chang*, UCLA

As one of the best dielectric, piezoelectric, and ferroelectric materials, PZT is a promising material to engineer nanoscale multiferroic composites. The magnetoelectric (ME) effect occurs indirectly through strain at the interface. Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, a thin film of PZT can be synthesized with precise control of the elemental composition (Zr/Ti = 52/48) and film thickness. ALD provides much superior uniformity and conformality over complex surface structures with high aspect ratios.

In this work, ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO_2, and TiO_2 layers using $Pb(TMHD)_2$, $Zr(TMHD)_4$, and $Ti(Oi-Pr)_2(TMHD)_2$ as metal precursors and H_2O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. ALD of PZT was studied to obtain (100) oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ on Pt (111) oriented platinized silicon substrates. In order to attain a highly oriented PZT thin film, a (100) textured $PbTiO_3$ seed layer was required because PZT orientation is generally governed by nucleation. The stoichiometry and crystallinity of PZT films were confirmed by XPS and XRD measurements. The conformality was confirmed over hollow Si_3N_4 cylinders with aspect ratio of 2.2.

By controlling the composition, thickness, and conformality of ALD PZT thin films, the properties of PZT can be exploited to increase the ME coefficient. Specifically, PZT was coupled with MgO/CoFeB to fabricate magnetic tunnel junction for memory applications. With co-mediated effects from higher dielectric constant and strain transfer via the interface, the voltage-controlled magnetic anisotropy effect is expected to increase, thereby realizing magnetic anisotropy energy per area per electric field greater than 37 fJ/(V·m) (Zhu, J. et al., *Phys Rev Lett.*, 108, 2012). ALD PZT thin films were shown to uniformly coat the walls of nanoscale porous CFO template to form a 3-D composite and a larger ME coefficient is expected due to an increase in surface area to volume ratio.

9:20am **TF+PS-TuM5 Atomic Layer Deposition Enabled Synthesis of Nanoscale Multiferroics**, *Calvin Pham*, *Y. Kim, J.P. Chang*, University of California at Los Angeles

Complex metal oxides exhibit remarkable tunability in their ferromagnetic, ferroelectric, and multiferroic properties that enable future applications such as non-volatile memory, miniaturized antenna, sensors and actuators. Nano-composites based on a magnetostrictive ferro/ferrimagnet paired with a piezoelectric have shown unique multiferroic behavior from effective strain-coupling at the interface. Motivated by the promise of high magnetoelectric coupling from nanostructured multiferroics, an atomic layer deposition (ALD) process was developed to synthesize $CoFe_2O_4$ (CFO) and $BiFeO_3$ (BFO), thereby enabling the formation of 2-D multilayered films with nanometer scale precision, as well as 3-D composites based on a mesoporous template. The highly conformal coating of ALD, due to self-limiting surface reactions, promises an intimate interface of the various ferroic phases to realize tunable magnetoelectric coupling by nano-texturing.

In this work, a radical enhanced ALD process was used to synthesize the complex oxide nano-structures, using metallorganic precursors $Bi(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Co(tmhd)_2$, and $Fe(tmhd)_3$ and oxygen atoms produced from a microwave power atomic beam source. The processing-structure-property relations were systematically studied. First, the nucleation delay for the initiation of the growth of one constituent oxide on another was quantified and a variety of process conditions were

systematically examined to assess the effects of process temperature, precursor pulsing time, and precursor pulsing ratio on film composition, growth rate, and structure. The ALD BFO and CFO films were confirmed to be conformal and of the exact stoichiometry with a linear growth rate, and their individual ferroic responses are comparable to those reported in literature, as synthesized by other techniques. The 2D BFO/CFO multilayers were synthesized with each layer measuring between 2-50 nm each, while the 3D composites consisted of mesoporous templates with ~15 nm diameter pores that were filled with ALD films. The attainable magnetic, ferroelectric, and magnetoelectric properties, including magnetoelectric coupling, are shown to be sensitive to the composition, morphology and microstructure of the composites as they interrelate and affect the strain state at the interface.

9:40am **TF+PS-TuM6 Laser Assisted Electron Beam Induced Deposition: Towards a Nanoscale Atomic Layer Deposition Process**, *Michael Stanford*, *B.B. Lewis, J.H. Noh,* University of Tennessee, *H. Plank,* Graz University of Technology, Austria, *J. Fowlkes,* Oak Ridge National Laboratory, *N.A. Roberts,* Utah State University, *P.D. Rack,* University of Tennessee

Electron beam induced deposition (EBID) is a direct-write process which can be used to selectively deposit material with nanoscale resolution. EBID utilizes a scanning focused electron beam to dissociate adsorbed precursor molecules which subsequently condense onto the substrate. One of the major limitations of the EBID process is low material purity resulting from incomplete by-product removal of the typically organometallic precursor. Therefore, the development of EBID purification strategies for enhanced materials functionality is a grand challenge for wider application of this synthesis technique. While recently EBID deposits have been used as selective atomic layer deposition catalyst, here we demonstrate an in-situ ALD-like process driven by electron and laser-induced thermal half reactions. We have developed an O_2-assisted laser anneal process to enhance the purity of patterns deposited using $MeCpPt^{IV}Me^3$ precursor gas. Additionally, we have demonstrated a laser assisted electron-beam-induced-deposition (LAEBID) process as an effective method to provide *in-situ* purification during deposition. The synchronized process is initiated by an approximately monolayer EBID cycle followed by a laser pulse which thermally desorbs by-products of the condensed phase. The process is repeated until the desired shape and size is achieved. The addition of a reactive O_2 gas and a synchronized electron and laser pulse begins to look a lot like a nanoscale atomic layer deposition process (ALD), however the half reactions are electron and thermally stimulated, respectively. We will demonstrate how factors such as laser pulse width, laser duty cycle, EBID beam current, and EBID dwell time have significant effects on the laser anneal and LAEBID processes. Importantly, the carbon reduction and apparent densification lead to higher resolution relative to standard EBID.

11:00am **TF+PS-TuM10 Effect of Film Stress on the Shape of Nanostructures Grown Using Atomic Layer Deposition**, *Jonas Gertsch*, *N.T. Eigenfeld, J.M. Gray, V.M. Bright, S.M. George,* University of Colorado, Boulder

Controlling the shape of nanostructures is crucial to the performance of nanodevices. Nanostructure shape can be tuned by varying stress in the various films that comprise the nanostructure. In this work, we explore the shape of $Al_2O_3/W/Al_2O_3$ trilayers fabricated using Al_2O_3 ALD and W ALD. Trilayer films were initially grown on polyimide molds that were formed into free standing "umbrella" nanostructures after processing and release. Depending on the stresses in the trilayer films and the thicknesses of the individual layers, the nanostructures can either remain flat or may curl up or down. The resulting shape can be controlled by varying the thicknesses of the individual Al_2O_3 ALD and W ALD layers in the trilayer. These "umbrella" nanostructures may be useful for microbolometer and other microelectromechanical systems (MEMS) applications. Additional studies will present stress measurements using atomic force microscope (AFM) investigations of ALD films in fixed-fixed and fixed-free cantilever structures.

11:20am **TF+PS-TuM11 Atomic Layer Deposition and Nucleation on Metallic Nanostructures for Plasmonic Devices**, *Jie Qi*, *X. Jiang, B.G. Willis,* University of Connecticut

Atomic layer deposition (ALD) has become an important technique for the deposition of nanometer thin dielectric and metallic thin films with applications in semiconductors, nanotechnology, catalysis, and energy. In particular, nanoscale metallic structures are gaining importance for fabrication of plasmonic antenna with applications in biochemical sensors, photocatalysis, and solar energy harvesting devices. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size and shape of the nanostructure. ALD offers a unique means to control the size, composition, and particle-particle junctions of nanostructures with high precision. The latter is particularly important for

creating hot spots where electric fields are strongly enhanced. A key challenge for ALD is the strict control of film composition and uniformity. Although a number of works have been published on the uniformity and layer by layer growth of amorphous dielectric thin films, the crystalline structures of metals present significantly increased complexity. Moreover, when seed layers, prefabricated nanostructures, or particles are involved, the sensitivity of film growth to surface structure has received relatively little attention so far.

In this work, we study the effects of surface preparation and seed layer properties on ALD Cu thin films relevant to plasmonic devices. Pd and Pt are used as seed layers for both planar thin films and two dimensional nanostructures. ALD growth was studied for different sized nanostructures and surface preparations including: e-beam deposition, high temperature annealing, solvent cleans, and UV/Ozone (UVO) pretreatment, as well as different ALD growth conditions. Samples were analyzed by XPS, SEM, AFM, EDS, and other techniques to compare film uniformity and surface structures. A strong dependence of Cu ALD growth quality was found for different nanostructures and surface preparations. Nucleation of Cu was greatly enhanced when UVO pre-treatment was performed on e-beam evaporated seed layers, but AFM results showed surface roughness increased with UVO cleaning time, which indicates rough, non-uniform growth. Seed layer thickness also played a role and it was observed that smoother and more uniform Cu thin films are obtained with thinner seed layers. Overall, planar thin films are poor models for nanostructure growth. Nanostructures are significantly more sensitive to surface preparations and growth conditions because of the similar length scales of nuclei and nanostructure size.

11:40am **TF+PS-TuM12** **Infrared and Thermoelectric Power Generation in Thin Atomic Layer Deposited Films**, *Harkirat Mann, B.N. Lang, Y. Schwab,* James Madison University, *J. Petteri-Niemelä, M. Karppinen,* Aalto University, Finland*, G.S. Scarel,* James Madison University

A mechanism for alternative energy, thermoelectric (TE) power generation, converts a temperature difference across two junctions into an electric potential. Although not as energy-efficient as solar panels or wind turbines, this mechanism is used in a wide variety of fields, e.g. to recapture waste heat. Recently it was discovered that a solid state TE power generators respond differently to heat or infrared (IR) radiation [1, 2]. To test the robustness of this finding, this research compares TE and IR power generation in the case of a nanometric TE device in which the active element is a thin TE film. The thin TE film is a 70 nm thick n-type Nb-doped titanium oxide film deposited by atomic layer deposition (ALD) onto a borosilicate glass substrate [3]. The interactions observed with heat show a linear relationship between temperature and voltage, whereas in IR radiation this linear relationship is broken down. The efficiency and the voltage stability obtained with the thin TE film is larger than that obtained by closing the electric circuit without the thin TE film. The possibility of using thin ALD films for IR power generation suggests that in the future the response to IR radiation can be tuned by exploiting the properties of the thin atomic layer deposited TE films.

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12:00pm **TF+PS-TuM13** **Atomic Layer Deposition of Tin Doped Titanium Oxide on Type-V Titanium Implant Surface for Enhanced Photoactivated Antibacterial Property**, *S.K. Selvaraj, A. Butt, Christos Takoudis*, University of Illinois at Chicago

Atomic layer deposition (ALD) is used for the first time to modify type-V titanium (Ti-6Al-4V) surface, a commonly used dental and orthopedic implant material.[1] ALD of titanium oxide and tin doped titanium oxide thin films were deposited on Ti-6Al-4V disks to enhance photoactivated antibacterial property of its surface. Tetrakis(diethylamino)titanium (TDEAT) kept at 65 °C and tin(II)acetylacetonate ($Sn(acac)_2$) kept at 70 °C were used as titanium and tin sources, respectively. Custom built hot-wall flow-type ALD reactor was used to deposit antibacterial thin films at 200 °C substrate temperature and 0.5 Torr.[2,3] Different composition of tin doping was achieved by changing the number of tin oxide ALD cycles. X-ray photoelectron spectroscopy was used to study the composition and purity of the thin films. Films were found to have titanium, tin, oxygen and trace amount of carbon. Excellent composition tunability of the ALD process was achieved. The resultant films were studied for photoactivated antibacterial property using a gram negative Escherichia coli bacterial strain ATCC 8739. The ALD coated Ti-6Al-4V disks were immersed in bacterial

solution and illuminated with UV light for 3 min. Irradiated bacterial samples were plated on agar plate and incubated for 12 hours at 37 °C. Two fold increase in antibacterial property was achieved on ALD TiO_2 coated disks compared to uncoated (control) disks. Tin doping further increased the activity by about two fold. Any increase in tin composition beyond 15 atom % was found to have no effect on antibacterial activity.

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2D Materials Focus Topic
Room: 310 - Session 2D+AS+HI+MC+NS+PS+SP+SS-TuA

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Manish Chhowalla, Rutgers University

2:20pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA1 Layer-Dependent Electronic and Physical Structure of 2D van der Waals Crystals, *Richard Osgood*, Columbia University **INVITED**
Because of their weak Van der Waals interlayer bonding transition-metal dichalcogenide (TMDC) semiconductors can be fabricated into atomically thin two-dimensional (2D) crystals with substantial ~ 1-2 eV bandgaps. As one example, monolayer MoS_2 consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. The TMDC 2D system has attracted great interest because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands, i.e. 100's of meV, due to broken inversion symmetry, which makes TMDCs interesting for spin-physics physics and devices. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Recently we have made a series of direct observations of the thickness-dependent electronic-band and crystal structure of TMDCs of both exfoliated and CVD grown sample. Because of the relatively modest sample sizes we have used micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both the exfoliated and chemical-vapor-deposition-grown crystals; these measurements provide direct evidence for the shifting of the valence band maximum from gamma bar (Brillouin zone center) to kappa bar (Brillouin zone corner), as the sample thickness decreases from bulk to monolayer. Our initial results were with MoS_2 and are described in a preliminary way in Refs 1 and 2. Our TMDC experimental results are compared with rigorous DFT calculations of both the bands and the UV transitions matrix elements. The results show an evolution in band structure, which is consistent with an indirect-to-direct bandgap transition in going from few-layer to monolayer TMDC and can be attributed to changes in quantum confinement as the number of layer decreases. Our microARPES and, subsequently, higher resolution nanospectroscopy data provide clear measurements of the hole effective mass, the strain present in the monolayer crystal films, and the valence-band spin-orbit splitting. Our results explain the low hole mobility of monolayer MoS_2 compared to thicker MoS_2 and show clearly the strong orbit split energies. Our results, using nanoLEED and LEEM also provide insight into the structure and defects in monolayer films. Experiments using K-doping of single-crystal samples and resulting level shifts are also described.

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3:00pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA3 X-ray Photoemission and Electron Energy Loss Spectroscopy Investigation of the Band Gap and Band Alignment for h-BN and MoS₂ Materials and Interfaces, *Benjamin French*, J. Brockman, M. French, M. Kuhn, J.D. Bielefeld, S.W. King, Intel Corporation, E. Bersch, G. Bersuker, SEMATECH, J. DiStefano, Y.C. Lin, J.A. Robinson, Penn State University
Hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) are two dimensional (2D) materials of significant interest for future nano-electronic devices. Due to a wide band gap (~ 6 eV), close lattice matching (< 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of primary interest as a potential substrate and gate dielectric in graphene channel transistor devices. In contrast, MoS_2 is a 2D semiconducting material with a band gap of ~ 1.8 eV that is attractive as a possible complement or alternative to graphene for nano-electronic devices requiring a large band gap. A key property for the success of both h-BN and MoS_2 in such devices is the interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and chemically vapor deposited MoS_2. In combination, we have utilized reflection electron energy loss spectroscopy (REELS) to investigate the band gap of both h-BN and MoS_2 materials to deduce the conduction band alignment. We show that in many instances the valence and conduction band offsets are significant and favorable for MoS_2/h-BN transistor devices.

3:20pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA4 STM/STS Characterization of MoS₂ Monolayers and Nanostructures, A. Mills, C. Chen, Virginia Tech, Y. Yu, L. Cao, North Carolina State University, *Chenggang Tao*, Virginia Tech
Atomically thin molybdenum disulfide (MoS_2) and nanostructures have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. Especially, monolayer MoS_2, an atomically thin semiconductor with a direct band gap, as opposed to an indirect band gap in bulk MoS_2, has been demonstrated as field effect transistors, optoelectronic devices and chemical sensors. In our experimental study, Monolayer MoS_2 and MoS_2 triangular nanostructures are synthesized through a self-limiting chemical vapor deposition (CVD) approach. The precursor materials, $MoCl_5$ and sulfur, react at high temperatures to produce MoS_2 species and subsequently precipitate onto substrates to yield MoS_2 films and triangular nanostructures. Using scanning tunneling microscopy (STM), we have investigated the structural and electronic properties of monolayer MoS_2 grown on glassy carbon and triangular MoS_2 nanostructures on highly ordered pyrolytic graphite (HOPG). We will also discuss our scanning tunneling spectroscopy (STS) measurements on these structures.

4:40pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA8 Surface Characterization of Metal Oxide Layers Grown on CVD Graphene and Spin Precession Measurements, *Akitomo Matsubayashi*, University at Albany-SUNY, W. Nolting, University of Albany-SUNY, D. Sinha, University at Albany-SUNY, A. Jayanthinarasimham, J.U. Lee, University of Albany-SUNY, V.P. LaBella, University at Albany-SUNY
Ultra thin metal oxide films grown on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel for device applications. This is particularly important for graphene based spintronic devices as tunnel barriers between the ferromagnetic metal as a spin injector and graphene have been known to increase the spin relaxation time measured utilizing non-local detection technique of spin precession by avoiding the conductivity mismatch problem. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier. We will present a systematic study of aluminum oxide layers grown on CVD graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the 0.2 nm titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium. The I-V characteristic study performed to electrically evaluate the metal oxide and the preliminary results of non-local spin precession measurements will be also addressed.

5:00pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA9 Morphology of CVD-grown Hexagonal Boron Nitride on Cu Foils, *Karthik Sridhara*, W.G. Cullen, University of Maryland, College Park, J.K. Hite, Naval Research Laboratory, M.S. Fuhrer, Monash University, Australia, D.K. Gaskill, B.N. Feigelson, Naval Research Laboratory
Hexagonal boron nitride (h-BN) has grown into prominence as a dielectric for graphene heterostructures. h-BN and graphene have been grown using chemical vapor deposition on various transition metal substrates. Compared to graphene, the morphology of CVD-grown h-BN on Cu has not been as widely studied. Here, we present a systematic study of the morphology of hexagonal boron nitride (h-BN) grown on polycrystalline Cu foils by chemical vapor deposition. The growth of h-BN is performed at ~1000°C in atmospheric pressure CVD with Ammonia Borane (H3NBH3) as the precursor. The copper foils, used as catalytic substrates, are thermally annealed at ~1030°C for >5 hours prior to growth and cooled slowly following growth termination. We utilized Ultra-high vacuum Scanning Tunneling Microscopy (STM), ambient AFM and SEM to assess the morphology of the CVD grown h-BN films. Highly symmetric single

crystallites of h-BN are observed for sub-monolayer growth, in agreement with recent reports. We consistently observe a corrugated topographic structure within the h-BN crystallites which is distinctly different from the surrounding copper surface, and this is consistently seen in STM, AFM, and high-resolution SEM. Our aim is to understand the nature of this difference and whether it might be due to effects of differential thermal contraction between h-BN and copper. However, complications arise due to possible changes in the copper substrate topography post-growth due to surface oxidation of the copper. Preliminary results with lateral force microscopy (LFM, frictional mode) show that these corrugations are unidirectional in a single Cu grain irrespective of the orientation of the h-BN crystal and generate frictional forces 200% greater than on the surrounding copper surface, reminiscent of earlier reports of unique frictional behavior in atomically-thin membranes [1]. STM and AFM are also used to study the twin crystal boundaries of h-BN. Preliminary STM observations indicate that merging h-BN crystals consistently have a gap of about 5 nm between them. The results of this study are independent of small variations of growth conditions.

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5:20pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA10   Influence of Chemisorbed Oxygen on the Growth of Graphene on Cu(100) and Cu(111) by Chemical Vapor Deposition, *EngWen Ong*, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *T.R. Mowll, P. Tyagi*, University at Albany-SUNY, *H. Geisler*, SUNY College at Oneonta, *C.A. Ventrice, Jr.*, University at Albany-SUNY

The influence of chemisorbed oxygen on the growth of graphene by catalytic decomposition of ethylene in an ultra-high vacuum (UHV) chamber on both the Cu(100) and Cu(111) surfaces has been studied. A custom UHV compatible heater stage was constructed that allows heating of a crystal to temperatures as high as 1000 °C at hydrocarbon pressures of up to 100 mTorr. System recovery to the low 10^{-10} Torr range is achieved within a few minutes of opening the gate valve to the turbo pump. The crystal structure of the graphene films was characterized with in-situ low energy electron diffraction (LEED), and the growth morphology was monitored by ex-situ scanning electron microscopy (SEM). For the clean Cu(100) substrate, heating from room temperature to the growth temperature while dosing with ethylene resulted in the formation of epitaxial graphene films. The crystal quality was found to depend strongly on the growth temperature. At 900 °C, well-ordered two-domain graphene films were formed. For the Cu(111) surface, heating from room temperature to the growth temperature while dosing with ethylene did not result in the formation of graphene. This is attributed to the lower catalytic activity of the (111) surface and the relatively high vapor pressure of the Cu surface. The use of an Ar overpressure to suppress Cu sublimation during the growth resulted in the formation of predominately single-domain epitaxial graphene films. Predosing either the Cu(100) or Cu(111) surface with a chemisorbed layer of oxygen before graphene growth was found to adversely affect the crystal quality of the graphene overlayers by inducing a much higher degree of rotational disorder of the graphene grains with respect to the substrate. The SEM analysis revealed that the nucleation rate of the graphene islands dropped by an order of magnitude after predosing either the Cu(100) or Cu(111) surface with a chemisorbed oxygen layer before growth. On the other hand, the average area of each graphene island was observed to increase by at least an order of magnitude. Therefore, the presence of oxygen during graphene growth affects both the relative orientation and average size of grains within the films grown on both substrates.

5:40pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA11   Novel Materials Properties at Atomically Thin Limit, *Zhi-Xun Shen*, Stanford University **INVITED**

In this talk, I will discuss recent progresses in uncovering novel materials properties at ultra-thin limit, with focus on mono-unit-cell superconductor FeSe and semiconductor MoSe2 respectively.

The observation of a large superconducting-like energy gap which opens at temperatures up to 65 K in single unit cell (1UC) thick iron selenide films on SrTiO3(FeSe/STO) has generated tremendous interest. A challenge is to understand the cause of enhanced Cooper pairing strength in this system, and possibly increase superconducting Tc. In this talk, we show angle-resolved photoemission spectroscopy, mutual inductance, and other measurements on 1UC and multi-UC thick FeSe films grown on Nb-doped SrTiO3. Our data provide clear evidence for strong cross-interface electron-phonon coupling in single UC, raising the possibility that large pairing gap are caused by the strong coupling between the FeSe electrons and certain

collective modes of SrTiO3. This suggests a pathway of "integrated functional components" approach to boost superconducting properties.

The intense interest of quantum systems in confined geometries is further amplified by the recent discovery of large enhancement in photo-luminescence quantum efficiency and a potential route to "valleytronics" in atomically thin layered transition metal dichalcogenides (TMDs) MX2 (M = Mo, W; X = S, Se, Te), which are closely related to the indirect to direct band gap transition in the single layer limit. Using angle-resolved photoemission spectroscopy (ARPES) on high quality thin film samples of MoSe2 grown by molecular beam epitaxy (MBE), we have made a direct observation of a distinct transition from indirect to direct band gap as the thickness of the sample is reduced to a monolayer. The experimental band structure indicates a stronger tendency of monolayer MoSe2 towards direct band gap with larger gap size than theoretical prediction. A comparison of directly measured ARPES band gap and optical data led to important new insights on semiconductor physics in 2D. Moreover, our finding of a significant spin-splitting of ~180meV at the valence band maximum (VBM) of a monolayer MoSe2 film could greatly expand its possible application in spintronic devices.

If time permits, I will also discuss the superconductivity in CaC6 and its implication on a possible pathway for superconducting graphene.

Plasma Science and Technology
Room: 308 - Session PS-TuA

Advanced BEOL/Interconnect Etching
Moderator: Toshihisa Nozawa, Tokyo Electron Ltd.

2:20pm PS-TuA1 Highly-Selective Etch Gas Chemistry Design for Precise DSAL Dry Development Process, *Hisataka Hayashi*, T. Imamura, H. Yamamoto, I. Sakai, M. Omura, Toshiba Corporation Center for Semiconductor Research & Development, Japan **INVITED**

To meet the needs of the device scaling trend, patterning technologies for critical dimension control less than 20 nm is required. For 1X nm pattern formation beyond the conventional optical lithography limit, it is necessary to use double (or multiple) patterning process which increases the process cost. Directed-self assembly (DSA) of block copolymer is one of the most attractive candidates for 1X nm pattern formation process and 12.5 nm hp patterns were formed using polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) [1]. DSA lithography (DSAL) process using PS-b-PMMA needs selective removal of PMMA to PS, which is called "development process". A wet development process was applied successfully for contact hole shrink process [2]. Although this method can remove PMMA selectively, pattern collapse will occur for line and space pattern resulting from surface tension of developer solvent.

On the other hand, although a dry development process is expected to solve this problem, selective removal of PMMA is difficult because PMMA is a similar organic polymer to PS. Dry development processes using Ar plasma and O_2 plasma have been reported and their selectivities were 3.9 and 1.7, respectively [3]. However in our case, higher selectivity is needed for etching the underlayer with PS as mask.

In this study, we focused on differences of material composition of PS and PMMA. Our results concluded that the control of ion energy and design of gas chemistry were key factors for the selective etch.

The aromatic group in PS is more durable than the carbonyl group in PMMA for ion bombardment. A selectivity of around 8 was achieved by the control of ion energy in xenon plasma.

PMMA has more oxygen in the film than in PS, so we designed the gas chemistry to realize the selective PMMA etch by using this difference of the oxygen content. We studied carbon containing gas plasma, because carbon radical will deposit on PS which does not contain oxygen. On the other hand, carbon radical will react with the oxygen in the PMMA to make volatile CO_x, therefore selective PMMA etch to PS can be realized. A selectivity of over 20 was realized using CO gas plasma [4].

DSA lithography dry development was successfully realized by controlling ion energy and designing the etching gas chemistry based on the difference of material composition of PS and PMMA.

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3:00pm PS-TuA3 Plasma Etch Considerations for Roughness Improvements during EUV and DSA Pattern Transfer using Mid Gap CCP, *Vinayak Rastogi, H. Matsumoto, A. Metz, A. Ranjan, N. Mohanty, A. Ko, Y. Chiba*, TEL Technology Center, America, LLC, *X. Hu, L. Wang, E. Hosler, R. Farrell, M. Preil*, GLOBALFOUNDRIES U.S. Inc.

As the semiconductor manufacturing industry is gearing toward sub-30nm technology nodes, there are continuous efforts to establish alternative patterning strategies other than optical lithography. Extreme Ultraviolet (EUV) Lithography, 193nm Immersion augmented with multiple patterning schemes ('Self Aligned Double Patterning – SADP', 'Self Aligned Quadruple Patterning – SAQP') and 'Directed Self Assembly – DSA' are considered to be promising candidates. However, these methodologies come with challenges posed in the form of polymer to polymer selectivity, mask budget, incoming defectivity, mask shape, critical dimension control, line edge roughness (LER) and line width roughness (LWR) of ever decreasing feature sizes. These issues can be addressed by using spatially uniform low density plasma obtained in a dual frequency mid-gap capacitively coupled plasma etcher.

Here, the unique advantages of TEL Etch Systems and parametric considerations is demonstrated to reduce LER and LWR during plasma etch pattern transfer for two example cases, EUV resist patterning for contact hole patterning and Directed Self Assembly of PS-b-PMMA system for line space patterning. Since mask thickness is much thinner as compared to currently used deep ultraviolet lithography (DUV) resist, both systems require high resist/polymer selectivity during plasma etch of patterns. Also, fine ion/radical flux ratio tunability is required to maintain the pattern profile. Direct current superposition (DCS) on capacitive-coupled plasma (CCP) can enhance the etch resistance of resist and it can improve contact edge roughness (CER). In the case of an applied DCS cure, we confirmed EUV resist etch resistance enhancement and CER improvement. Additionally, we investigated which parameter is dominant for EUV resist cure. For DSA related etching, we have successfully demonstrated pattern transfer into metal hard mask for BEOL application and non-metal hard mask for FEOL applications using TEL Etch Systems. Specifically, the effect of deposition rich gases is investigated for preferential passivation of mask during etching of PS-PMMA films in an oxidizing plasma. This work was performed by the research teams of Tokyo Electron and GLOBALFOUNDRIES at Albany Nanotech Development Facilities.

4:20pm PS-TuA7 Interactions between the Plasma and the Mask Material during Contact Etching, *Mokrane Mebarki*, STMicroelectronics, France, *M. Darnon*, LTM - MINATEC - CEA/LETI, France, *C.J. Jenny, D. Ristoiu*, STMicroelectronics, France, *N. Posseme*, Cea-Leti, Minatec, *O. Joubert*, LTM - MINATEC - CEA/LETI, France

The reduction of device dimension at the sub-15nm technological node requires the use of double patterning for contact etching. Line and space patterns are defined first in a thin TiN layer. Then, a trilayer stack with Si-containing anti reflection coating (SiARC) and organic planarizing layer (OPL) is used to define open areas. The mask is defined by the intersections of both hard mask of TiN and OPL patterns and is used to etch contacts into silicon oxide (TEOS).

The OPL mask must conserve straight profiles during the different etching steps and TiN is exposed to the plasma during silicon oxide etching. The OPL can be etched by different plasmas (N_2/H_2, O_2/SO_2, O_2/CO_2) that may induce a passivation layer on the sidewalls via different passivation elements such has CN, CS, CO. Such passivation layers, as well as the presence of TiN during contact etching, can interfere with the SiO_2 etching process and change the final pattern profile. In this study, we investigated the OPL mask etching in COS/O_2 plasma in comparison with N_2/H_2 plasma.

The XPS analyses are performed into Theta300 angle resolved XPS system from Thermo Scientific, ellipsometry measurements are done with spectra FX 200th multiwavelength ellipsometer from KLA-Tencor and OES spectra are recorded with a SD1024 spectrograph detector from SpectraView.

Electronic microscopy observations of OPL patterns etched in N_2/H_2 or in COS/O_2 with various COS/O_2 ratios show that straight profiles without undercut can be obtained. After SiO_2 etching using a fluorocarbon-based plasma, we observe strong profiles variations in the SiO_2 depending on the OPL etch process. After the COS/O_2 OPL open, during the first seconds of the SiO_2 etching, strong emission lines originating from CS species are observed by OES. In addition, EDX analyses after COS/O_2 OPL etching reveal a large amount of sulfur on OPL sidewalls and TiN surface. TiN mask profile is also degraded during the over etch of the OPL and Ti residues are redeposited on all the surfaces. To precise the interaction mechanisms, XPS analyses are performed on TiN, OPL and TEOS after exposure to the various OPL etching processes. We evidenced that the contact profile is influenced by both the process used during OPL opening and the presence of TiN on the wafer. Degradation of masks profiles leads to Ti or S containing residues formation which tends to block the SiO_2

etching. These effects can be reduced by an increase of COS/O_2 ratio during OPL etching.

4:40pm PS-TuA8 Contact Level Patterning Challenges for Sub 22-nm Architecture, *Jeffrey Shearer, J. Dechene, S. Kanakasabapathy*, IBM Corporation, *N. Mohanty, B. Messer, H. Cottle, A. Metz*, TEL Technology Center, America, LLC, *J. Lee*, Samsung Electronics

As gate pitch scaling continues past the 22nm node, we are approaching gate and contact pitches below the threshold of single-exposed lithography. One has to decompose the contact layer into multiple reticles and integrate them on the wafer to achieve an effective pitch less than this threshold. Such integration schemes bring with them issues with substrate damage and gate-contact shorts. Although exercised in BEOL patterning schemes, multicolor integration schemes require customization for the contact module. Damage from plasma exposure to the gate sidewall and source/drain in multiple color integration schemes can detract from gate to contact short yield and device yield. This paper will present innovative etch-integration cooptimization options to minimize plasma induced damage. We also highlight the process challenges in pattern fidelity that the industry has to surmount to make these manufacturable as well as RIE strategies that will help overcome these challenges. Hard mask memorization will be discussed for contact level integration as well as how material selection and etch process optimizations are needed to ensure pattern robustness. Specifically, data will show that multicolor processing causes earlier colors to have degraded device performance. A metal hard mask memorization scheme will be discussed as a way to alleviate multiple source/drain plasma exposures during product processing, thereby improving device yield.

5:00pm PS-TuA9 Method for Preferential Shrink Ratio Control in Elliptical Contact Etch, *Hongyun Cottle, A. Lisi, A. Metz, K. Kumar, D. Koty, A. Mosden, P. Biolsi*, TEL Technology Center, America, LLC

Sub-22nm logic technology requires contact level etch to meet aggressive critical dimension (CD) shrinks as ArF immersion pattering has mostly reached its resolution limit. Utilization of elliptical contacts brings new constraints to CD shrink. Controlling the 2-D aspect ratio of oval contacts is critical to both device performances and yield. One challenge is that conventional plasma etch shrink methods can induce more shrinkage in the major (Y axis) direction than the minor (X axis), which can cause line-end shortening and feature tip-to-tip spacing control problems.

This paper presents a unique dry etch process that yields a Y to X shrink ratio range ≤1 concurrent with a 50% CD reduction from lithography. By utilizing a direct current superposition (DCS) technology, along with CxHyFz chemistry to cure a negative tone developed photoresist (NTD), this method creates a controllable *in-situ* hydrocarbon deposition, which is mainly responsible for the Y to X shrink ratio range ≤1. This is not seen with conventional fluorocarbon etch based shrink where Y/X shrink ratio is typically >1, as a result of the larger collection angle for gas phase deposition along the major axis. The Y/X shrink ratio range can be modulated through process condition such as gas ratio, pressure, time, etc. After the controllable hydrocarbon deposition, multiple mask defining transferring steps can be executed anisotropically to complete the pattern transfer. Reported is the structural characterization pre and post etch detailing shrink ratio control. In addition, a mechanistic model will be proposed based on optical emission spectroscopy (OES), thin film compositional analysis, and mass spectrum data.

5:20pm PS-TuA10 Novel Fluorocarbons Chemistries to Enable 3D NAND High Aspect Ratio Etching, *R. Gupta, B. Lefevre, Venkateswara Pallem, N. Stafford*, American Air Liquide, *J.M. Kim, K. Doan, S. Nemani*, Applied Materials Inc.

The development of high aspect ratio etch processes is one of the challenges that must be overcome for the next generation devices such as 3D NAND. In addition to tool improvements a new variable for optimization of the process is the fluorocarbon chemistry (FC) that is used. The study presented here examines the effect of different FC on high aspect ratio etch processes. In this study several novel fluorocarbons chemistries have been tested using a 200mm dual frequency CCP etch tool. Novel chemistries are used to etch planar film of SiO2, amorphous carbon, and SiN for which etch rates are measured as well as the deposition rate on bare Si. The O2 flow rate is varied in order to find the optimum ratio of etch gas to O2. High aspect ratio structures with oxide/nitride stack are etched using optimum condition. SEM cross-sections of pattern structures were analyzed to determine chemistry effect on etch profile, selectivities and mask preservation. By varying F:C ratios and molecular structures, high aspect ratio structure (>25) were obtained with sub 100nm features with improved profile compared to standard FC chemistry. Mass spectrometry was also performed on pure etch gas. Variation of the electron energy from 10 to 100eV gives fragments concentration which can help to predict fragmentation of the

molecules under plasma condition and etch performance of molecules. The most promising chemistry was tested on Applied Materials 300mm Dielectric Etch tool.

5:40pm PS-TuA11 LER/LWR Improvements in Dual Frequency CCPs for Advanced Node Patterning, *Mingmei Wang*, N. Mohanty, S. Nakamura, A. Ko, A. Ranjan, TEL Technology Center, America, LLC

One of the key parameters in semiconductor mass production control is Line Edge Roughness (LER) / Line width roughness (LWR) owing to its direct contribution to gate length variation, edge placement error, line resistance variation and others. Due to the resolution-line edge/width roughness-sensitivity (RLS) trade-off for photoresists (PR), photolithography has reached its limit to further improve PR LER/LWR for advanced technology nodes (1xnm and beyond). Thus post lithography roughness reduction treatments have become critical in meeting the ITRS targets for LER/LWR. Vacuum Ultra Violet (VUV) treatment has been showing promising results with photochemical modification based smoothening of PR surface using gases like Ar, H₂, HBr etc. which can produce VUV radiation. While several studies have been published over the past decade for improving PR LER/LWR using VUV, most do so by analyzing the results post-VUV-treatment at resist level (before etch transfer). To get good LER for final pattern, pattern transferring from PR is also critical.

CCP chambers, by design, have advantages to achieve good LER/LWR due to the relatively low plasma density and high deposition/etch radical ratio. CCPs with a wide gap are able to well decouple top and bottom RF powers so that we have either low plasma density with high ion energy incident onto the wafer surface or vice versa. In this presentation, post etch LER/LWR data will be discussed with various approaches, such as different treatment duration, different gas combination, ratio plus DC superposition, PR margin, and different plasma parameter settings etc. We will demonstrate that in-order to meet the ITRS targets for LER/LWR for 1x nm and beyond requires co-optimization of the resist roughness with resist profile; thickness; and the subsequent pattern transfer process onto underlying stack.

Thin Film
Room: 307 - Session TF+EN+PS-TuA

ALD for Energy
Moderator: Erwin Kessels, Eindhoven University of Technology, Netherlands

2:20pm TF+EN+PS-TuA1 Li-Based ALD Solid Electrolytes for Beyond-Li-Ion Batteries, *Alexander Kozen**, A.J. Pearse, M.A. Schroeder, C. Liu, M. Noked, C.F. Lin, G.W. Rubloff, University of Maryland, College Park

Solid Li-based inorganic electrolytes offer profound advantages for energy storage in 3-D solid state batteries: (1) enhanced safety, since they are not flammable like organic liquid electrolytes; and (2) high power and energy density since the solid electrolyte can support interdigitated nanostructured electrodes, avoiding binders, separators, and much larger spacing (tens of mm's) between fully separated electrodes. The quality of thin solid electrolytes – even in planar form – is currently a major obstacle to solid state batteries[1] restricting electrolyte thickness to >100 nm to control electronic leakage, consequently slowing ion transport across the electrolyte and impeding interdigitated 3-D nanostructure designs that offer high power and energy. Furthermore, the ion-conducting, electron-insulating properties of solid electrolytes are promising for their use as passivation or protective layers on metal anodes (Li, Na, Mg) and on cathodes in proposed "beyond-Li-ion" battery configurations such as Li-O₂ and Li-S.

Atomic layer deposition (ALD) is well suited to the challenge of solid electrolytes, providing ultrathin, high quality films with exceptional 3-D conformality on the nanoscale. We have developed ALD processes for Li₂O, Li₃PO₄, and LiPON from LiO^{t}Bu, H₂O, and N₂, exploiting spectroscopic ellipsometry, downstream mass spectrometry, and XPS surface analysis, all *in-situ*. Post-ALD XPS reveals for the first time carbon-free electrolytes and their intrinsic surface chemistry. E.g., ALD Li₂O grown at 250C is reversibly transformed to LiOH upon exposure to H₂O, but transforms back upon annealing. LiOH is completely and irreversibly converted to Li₂CO₃ by CO₂ exposure. These kinds of observations are essential to developing process sequences for fabricating 3-D solid batteries.

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* TFD James Harper Award Finalist

We then demonstrate the impact of this solid electrolyte synthesis in several examples. For solid state batteries, we employ the electrolytes in planar and nanostructured battery configurations to determine their Li diffusivity and electrochemical performance. For beyond-Li-ion configurations with organic electrolytes, we show the use of ALD Li₂O at controlled mass loading in high aspect ratio Li-O₂ cathodes to elucidate the Li-O₂ charging chemistry, and we demonstrate the use of the ALD solid electrolytes in passivating Li anodes in Li-S batteries.

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2:40pm TF+EN+PS-TuA2 Engineering Lithium-Containing Ionic Conductive Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications, *Jea Cho*, T. Seegmiller, J. Lau, L. Smith, J. Hur, B. Dunn, J.P. Chang, University of California at Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications. These batteries have the potential to function as miniaturized power sources for microelectromechanical (MEMS) devices through the fabrication of 3-dimensional configurations. To fabricate a fully functional 3D Li-ion microbattery, however, an ultra-thin and highly conformal electrolyte layer is required to coat the 3D electrodes. The solid oxide Li-ion conductor, lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO), synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications owing its adequate ionic conductivity as well as improved electrode stability.

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating even on highly complex structures such as high aspect ratio 3D electrodes. The metal precursors, lithium t-butoxide (LTB), trimethylaluminum (TMA), tris(tert-butoxy)silanol (TTBS), and tetraethylorthosilicate (TEOS) were used to form Li$_x$Al$_y$Si$_z$O via ALD. *In-situ* FTIR was implemented to study the incubation time and growth mechanisms for each oxide deposited on the other to improve the controllability of the films. *In-situ* FTIR studies revealed that the growth mechanism of silicon oxide is strongly affected by the underlying oxide layer, exhibiting different surface reaction mechanisms during the incubation stage.

Li-ion conductivities and the activation energy for conduction of as-deposited LASO/LAO/LSO films were determined for different lithium contents and film thickness. The LASO ALD coating on 3D carbon array posts were confirmed to be conformal and uniform using transmission electron microscopy (TEM) imaging. A Li-ion half-cell consisting of LASO coated on 3D carbon array electrode showed reversible electrochemical behavior. Lithiation cycling tests of thin LASO/LAO/LSO films were found to be functions of both composition and thickness. The reversibility and kinetics of insertion as well as the effect on the cycling stability from the direct deposition of LASO/LAO/LSO on potential anode materials, SiNWs were also investigated using *in-situ*TEM observations during lithiation.

3:00pm TF+EN+PS-TuA3 Applications of ALD for Li ion Batteries and Low Temperature Fuel Cells, *Xueliang (Andy) Sun*, University of Western Ontario **INVITED**

Atomic layer deposition (ALD) is a novel and unique coating technique with many applications in energy storage and conversion [1]. In this talk, I will present our recent work on exploring the applications of atomic layer deposition (ALD) in both fuel cells and Li ion batteries [2-7].

In the first part, we will report of use of ALD for Pt catalysts used in low temperature fuel cells. In particular, atomic Pt or clusters prepared by ALD show ten times higher methanol oxidation properties compared with ETK commercially-used catalysts [2].

In the second part, we will focus on employing ALD as a surface-modification method to enhance the performance of LIBs. Different materials for surface-modification (such as Al₂O₃, ZrO₂, TiO₂ and AlPO₄) [3,4] were first developed by ALD. Then systemic studies were carried out by using those materials to modify the anode (Li₄Ti₅O₁₂, SnO₂) [5] and the cathode (commercial LiCoO₂, NMC) [6]. The effects of different coating materials on the LIB performance of the anode and cathode were investigated in details. In addition, the potential application of ALD as a powerful technique for preparing solid-state electrolyte will be demonstrated [7]. We will discuss further development of ALD for fuel cells and Li ion batteries.

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4:20pm TF+EN+PS-TuA7 ALD for a High Performance "All-in-One" Nanopore Battery, *Chanyuan Liu*, X. Chen, E. Gillette, A.J. Pearse, A.C. Kozen, M.A. Schroeder, K. Gregorczyk, S.B. Lee, G.W. Rubloff, University of Maryland, College Park

A self-aligned nanostructured battery fully confined within a single nanopore presents a powerful platform to determine the performance and cyclability limits of nanostructured storage devices. We have created and evaluated such structures, comprised of nanotubular electrodes and electrolyte confined within anodic aluminium oxide (AAO) nanopores as "all-in-one" nanopore batteries. The nanoelectrodes include metal (Ru or Pt) nanotube current collectors with crystalline V_2O_5 storage material on top of them, penetrating part way into the AAO nanopores to form a symmetric full storage cell, with anode and cathode separated by an electrolyte region.

The unprecedented thickness and conformality control of atomic layer deposition (ALD) and the highly self-aligned nanoporous structure of anodic aluminum oxide (AAO) are essential to enable fabrication of precision, self-aligned, regular nanopore batteries, which display exceptional power-energy performance and cyclability when tested as massively parallel devices (~2billion/cm^2), each with ~1μm^3 volume (~1fL).

To realize these "all-in-one" nanopore batteries, we focused on the precise control of Ru and Pt thin film conformality inside very high aspect ratio (300:1) AAO nanopores by thermal ALD process. 7.5nm thick Ru and Pt are optimized to be 15μm deep at both sides of 50μm long AAO pores in order to provide fast electron transport to overlying V_2O_5 at both anode and cathode sides, while keeping them spatially and electrically isolated. Active storage layers of 23nm thick crystalline V_2O_5 were deposited inside the metal nanotubes to form core-shell nanotubular structures at low temperature (170°C) using O_3 as the oxidant, with <001> direction perpendicular to tube surface and RMS roughness ~4nm. Then the V_2O_5 was prelithiated at one end to serve as anode while pristine V_2O_5 without Li at the other end served as cathode, enabling the battery to be cycled between 0.2V and 1.8V and to achieve full theoretical Faradaic capacity of the V_2O_5. Capacity retention of this full cell at high power (relative to 1C rates) is 95% at 5C and 46% at 150C rates (i.e., 24 sec charge/discharge time). At 5C rate (12 min charge-discharge cycle), 81.3% capacity remains after 1000 cycles. These performance metrics are exceptional, exceeding those of most prototypes reported in the literature. These results demonstrate the promise of ultrasmall, self-aligned/regular, densely packed nanobattery structures as a building block for high performance energy storage systems.

4:40pm TF+EN+PS-TuA8 Pseudocapacitive Manganese Oxide Grown by Atomic Layer Deposition, *Matthias Young*, C.D. Hare, A.S. Cavanagh, C.B. Musgrave, S.M. George, University of Colorado, Boulder

Pseudocapacitive supercapacitors are a class of energy storage materials that are midway between lithium ion batteries and capacitors in terms of both power and energy densities. Manganese oxide is a well-known pseudocapacitive material with particular appeal due to its earth abundance and low cost. In previous work, we have demonstrated that MnO ALD produced using bis(ethylcyclopentadienyl)manganese ($Mn(CpEt)_2$) and water can be electrochemically oxidized to produce pseudocapacitive MnO_2 in aqueous electrolytes. However, recent results have shown that the electrochemical oxidation of MnO ALD films results in partial dissolution and delamination. To avoid these problems, we have worked to grow pseudocapacitive MnO_2 by ALD that requires no post-processing. We have grown manganese oxide ALD films using ozone as the coreactant with $Mn(CpEt)_2$. We have also used intermediate ozone doses during $Mn(CpEt)_2$ and water exposures during ALD growth. The use of ozone results in more oxidized manganese oxide films. Another issue is that the alpha-MnO_2 crystal structure of MnO_2 which exhibits high pseudocapacitance contains open channels that are only stable in the presence of cations such as Na^+ or

K^+. Consequently, directing the ALD growth toward alpha-MnO_2 pseudocapacitive crystal structures requires the incorporation of an alkali metal into the MnO_2 ALD films.

5:00pm TF+EN+PS-TuA9 Excellent Chemical Passivation of p^+ and n^+ Surfaces of Silicon Solar Cells by Atomic Layer Deposition of Al_2O_3 and SiO_2/Al_2O_3 Stacks, *Bas van de Loo*, H.C.M. Knoops, Eindhoven University of Technology, Netherlands, *G. Dingemans*, ASM, Netherlands, *I.G. Romijn*, ECN Solar Energy, Netherlands, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Thin films of Al_2O_3 provide excellent passivation of heavily p-doped (p^+) silicon surfaces and are therefore often applied in silicon solar cells to reach high efficiencies. The high level of passivation by Al_2O_3 can be attributed to its low interface defect density and high negative fixed charge density Q_f. However, the negative fixed charge density of Al_2O_3 can be detrimental for the passivation of n^+ surfaces [1]. Furthermore, in advanced cell architectures such as interdigitated back-contact (IBC) solar cells, both n^+ and p^+ surfaces are adjacent and are preferably passivated simultaneously. To this end, we systematically study the surface passivation by SiO_2/Al_2O_3 stacks prepared by atomic layer deposition (ALD), which exhibit excellent chemical passivation while the effective fixed charge density can be tuned to zero by carefully tuning the SiO_2 thickness.

Al_2O_3 and SiO_2/Al_2O_3 film stacks with varying ALD SiO_2 thickness (0-12 nm) were prepared by plasma-enhanced ALD at 200°C, with $H_2Si(N(C_2H_5)_2)_2$ and $Al(CH_3)_3$ as metal-organic precursors and O_2 plasma as oxidant. Moreover, a SiO_2 ALD process using ozone was developed as this oxidant is more suitable for batch ALD. The relevant process parameters for surface passivation, such as ozone exposure time, were identified. The passivation of n^+ and p^+ doped surfaces was studied in detail, and results were compared with industrial passivation schemes, including PE-CVD SiN_x and similar SiO_2/Al_2O_3 stacks from a high-volume manufacturing ALD batch reactor.

A superior level of passivation of n^+ surfaces (R_{sheet} = 100 Ω/sq) was obtained by SiO_2/Al_2O_3 stacks as compared to single layer Al_2O_3, significantly reducing the recombination current density (J_0) from (81±10) to (50±3) fA/cm^2. On p^+ surfaces (R_{sheet}= 60 Ohm/sq), J_0 increases with increasing SiO_2 thickness. The results can be explained by an excellent level of chemical passivation, combined with a strongly reduced negative fixed charge density when increasing the SiO_2 thickness. To fully exploit the virtues of ALD, the concept of using SiO_2/Al_2O_3 stacks for the passivation of both the n^+ and p^+ doped surfaces in a *single* deposition run was demonstrated on (completed) n-type bifacial solar cells, reaching conversion efficiencies >19%. The results are promising for IBC solar cells, where n^+ and p^+ surfaces are adjacent and care must be to achieve a low surface recombination, high shunt resistance and industrial feasibility.

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5:20pm TF+EN+PS-TuA10 Opportunities for Transparent Conductive Oxides Prepared by ALD for Silicon Heterojunction Solar Cells, *Bart Macco*, S. Smit, Y. Wu, D. Vanhemel, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

In silicon heterojunction (SHJ) solar cells, transparent conductive oxides (TCOs) serve as the top window layer which provides lateral charge transport to the metal contacts whilst maintaining a high optical transparency. Commonly-employed TCO materials include Sn-doped indium oxide (In_2O_3:Sn), Al-doped zinc oxide (ZnO:Al) and more recently also H-doped indium oxide (In_2O_3:H)[1], which are typically deposited by sputtering. In this work, atomic layer deposition (ALD) is explored as an alternative deposition technique for the abovementioned materials. Three salient features of the ALD process will be addressed. Firstly, the applicability of these ALD TCOs is evaluated in terms of their optoelectronic performance. It is shown that through controlled ALD doping cycles the carrier density can be accurately tuned and a low resistivity (<0.5 $m\Omega cm$) required for SHJ solar cells can be obtained. Secondly, it is shown that a thermal ALD process does not induce damage to the underlying a-Si:H passivation layers found in a SHJ solar cell. This is a distinct advantage over the conventional sputtering technique, in which plasma-related (UV, ions) damage is known to reduce the passivation level of the a-Si:H layers.[2] This perk of ALD is put to use in bilayers of ALD ZnO:Al/sputtered In_2O_3:Sn, where a thin ALD TCO layer (<15 nm) can very effectively protect the a-Si:H layers from sputter damage. TEM and *in-situ* spectroscopic ellipsometry measurements show that the protective properties are strongly correlated with the TCO surface coverage, as the initial ALD TCO growth on the a-Si:H layer suffers from a nucleation delay and associated island-like growth.[3] Finally, the accurate control over the doping (profile) of the TCO offered by ALD opens up ways to optimize the band alignment of a SHJ solar cell. At the interface of the TCO and the p-type a-Si:H, a high doping of the TCO is unfavorable for the band

alignment and results in a reduced fill-factor.[3] On the other hand, the conductivity requirement of the TCO sets a lower bound to the doping level. In this respect, graded doping of the TCO by ALD allows for effective decoupling of the conductivity requirements of the TCO with the optimization of the interface contact formation.

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5:40pm TF+EN+PS-TuA11   Study of the Surface Passivation Mechanism of *c*-Si by Al$_2$O$_3$ using *In Situ* infrared spectroscopy, *R.P. Chaukulkar*, Colorado School of Mines*, W. Nemeth, A. Dameron, P. Stradins,* National Renewable Energy Laboratory*, **Sumit Agarwal**,* Colorado School of Mines

The quality of Si surface passivation plays an integral role in the performance of *c*-Si-based solar cells. Recently, Al$_2$O$_3$ films grown by atomic layer deposition (ALD) have been shown to be an effective passivant for *c*-Si surfaces with surface recombination velocities (S_{eff}) that are <5 cm/s. The chemical passivation of the *c*-Si surface via Al$_2$O$_3$ is achieved by a reduction in the defect density at the interface, while field-effect passivation is attributed to the fixed negative charge associated with the Al$_2$O$_3$ films. However, a post-deposition annealing step is required to achieve this high level of passivation. We have investigated the mechanism of chemical passivation during the annealing step using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Specifically, we have studied the role of residual H- and O-atom migration from the ALD Al$_2$O$_3$ films to the *c*-Si/Al$_2$O$_3$ interface. Using Al(CH$_3$)$_3$ and O$_3$ as the ALD precursors, Al$_2$O$_3$ films were deposited directly onto high-lifetime float-zone *c*-Si internal reflection crystals (IRCs) followed by thermal annealing at 400 °C in different atmospheres. Specifically, we have used D-terminated *c*-Si IRCs to differentiate the residual H atoms that may migrate from ALD Al$_2$O$_3$ films versus the residual D atoms present at the Al$_2$O$_3$/*c*-Si interface after ALD. Within the sensitivity of the ATR-FTIR spectroscopy setup of ~10^{12} cm^{-2} for Si-H bonds, we do not detect any migration of H from Al$_2$O$_3$ to the *c*-Si interface. Therefore, we conclude that the migration of O, and the subsequent restructuring of the interface during the annealing step, primarily contributes towards the chemical passivation of the Al$_2$O$_3$/*c*-Si interface. The ATR-FTIR spectroscopy measurements are complemented by the minority carrier lifetime, interface defect density, and built-in charge density measurements on SiO$_2$/Al$_2$O$_3$ stacks on *c*-Si, which enable us to isolate chemical passivation from field-effect passivation. The stacks were annealed in different atmospheres to better understand the role of O versus H atoms in the chemical passivation mechanism.

6:00pm TF+EN+PS-TuA12 Low Temperature Plasma-assisted Atomic Layer Deposition of TiO$_2$ Blocking Layers for Flexible Hybrid Mesoscopic Solar Cells, *V. Zardetto,* Eindhoven University of Technology, Netherlands*, F. di Giacomo, T.M. Brown, A. di Carlo, A. D'Epifanio, S. Licoccia,* University of Rome "Tor Vergata", Italy*, W.M.M. Kessels, **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Atomic Layer Deposition (ALD) is widely acknowledged in the field of c-Si and thin film PV technologies, for the fabrication of ultra-thin, uniform and conformal layers.[1] Thermal ALD has been applied also in the case of more challenging interfaces, e.g. dye-sensitized solar cells (DSCs) and the novel hybrid organo-lead-halide perovskite solar cells. Particularly, TiO$_2$ blocking layers have been developed on glass/TCO substrates with the aim of decreasing the charge recombination processes at the interface between the ITO and the mediator. Recently, we have explored the benefit of plasma-assisted ALD (PA-ALD) in terms of low temperature processing applied to flexible DSCs for the development of highly transparent Pt counterelectrodes on ITO/PEN. [2] In this work, we further explore PA-ALD for the deposition of ultra-thin, highly compact TiO$_2$ blocking layers on ITO-polymer substrates for DSCs and perovskite solar cells. The layers were prepared in a remote plasma reactor (FlexAL^{TM}) at 150 °C using an heteroleptic alkylamido precursor Ti(Cp^{Me})(NMe$_2$)$_3$ alternated with an O$_2$ plasma. For DSCs with an iodide-based electrolyte, the introduction of the blocking layer is essential at low light intensity, in order to increase the indoor performance of the cell. It is found that the presence of ultra-thin (6 nm) TiO$_2$ layers slightly affects the performance of the cell under sun simulator, whereas it definitely improves the generated power (+40%) under low level illumination (300 lux). The blocking behaviour of the PA-ALD deposited TiO$_2$ towards the tri-iodide reduction has been investigated by electrochemical impedance spectroscopy and Tafel plot analysis. We pinpointed that an increase in the TiO$_2$ layer thickness above 6 nm leads to a

decrease of the recombination processes at the TCO/electrolyte interface, as well as to a dramatic reduction of the electron collection at the TCO, accompanied by a decrease in cell performance. For mesostructured perovskite (CH$_3$NH$_3$PbI$_2$Cl- based) solar cells, the application of a TiO$_2$ blocking layer is essential for the performance of the device, due the higher current exchange at the interface TCO-hole transport material, i.e. Spiro-OMeTAD, typically used in this architecture. The application of a 11 nm-thick TiO$_2$ layer resulted in an efficiency of 7.4%. In conclusion, ALD is a valid approach for controlling electrochemical charge-transfer processes in mesoscopic solar cells.

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

Plasma Science and Technology Poster Session

PS-TuP3   Optical Emission Spectroscopy of CH_3F/CO_2 Plasmas and Etching of SiN_x and p-Si, *Qiaowei Lou, S. Kaler, D.J. Economou, V.M. Donnelly*, University of Houston
CH_3F plasmas are widely used in selective SiN_x etching over Si or SiO_2 with additives like O_2 or CO_2. In this work, inductively coupled CH_3F/CO_2 discharges were studied by optical emission spectroscopy (OES), with rare gas actinometry, as a function of feed gas composition and power (5–400 W), at a constant pressure of 10 mTorr. SiN_x(300 nm on Si) and Si (10 nm on Ge) etching was also studied in "plasma beams" created from both CH_3F/CO_2 and CH_3F/O_2 feed gases. Surfaces and film thicknesses were characterized *in situ* by vacuum-transfer XPS, and *ex situ* by spectroscopic ellipsometry. An abrupt transition in H, F, and O number densities was observed when the CO_2 feed gas was increased above 74-80 vol. %, similar to the enhancement in the number densities of these species above 48% O_2 in CH_3F/O_2 plasmas. These step changes were ascribed to the transition from polymer-covered to polymer-free reactor walls as increasing O_2 or CO_2 additions cause the film etching rate to exceed the deposition rate. Absolute H, F, and O number densities increased with power in CH_3F/CO_2 (20%/80%) plasmas, reaching 0.24, 0.81 and 1.92 x10^{13}/cm^3, respectively, at 300W. This gas composition results in polymer-free wall conditions. Compared with CH_3F/O_2 (50%/50%) plasmas, the F and H number densities were lower and the O number density was higher in CH_3F/CO_2 plasmas. A maximum SiN_x etching rate (no bias) of 75 Å/min was observed using a plasma beam effusing from a 50%/50% CH_3F/O_2 compact ICP. A lower maximum SiN_x etching rate of 34 Å/min was found for CH_3F/CO_2 at 25%/75% composition.

PS-TuP5   Simulation and Diagnostic Study on the Large Area Magnetized Inductively Coupled $Ar/O_2/CF_4$ Plasma, *Ho-Jun Lee, E.-J. Son, Y.-G. Kim*, Pusan National University, Republic of Korea
Scaling up of inductively coupled plasma (ICP) and capacitively couple plasma (CCP) is important and urgent task for future 450 mm semiconductor wafer processing. A weakly magnetized inductively coupled plasma (MICP) have been introduced as an effort to improve efficiency, stability of low pressure operation and density uniformity of ICP. MICP is a source utilizing cavity mode of low frequency branch of right hand circularly polarized wave.[1] In the previous study, results on the simulation and optical multi-port diagnostics of Ar MICP have been presented.[2] In this study we present simulation and experimental results on the properties of ICP and MICP with Ar/CF_4, $Ar/O_2/CF_4$ chemistry. Flow field calculation of feed gas was included in the self-consistent plasma simulation. Electron density and energy was measured with tuned langmuir probes. Spatially resolved emission spectra were taken with a home-made, wafer type multi-channel optical emission measurement system. In 5 mtorr, Ar/CF_4(5~20%) discharge condition, electron density uniformity of MICP was improved about factor of two compared with that of ICP. Electron density of MICP in Ar/CF4 discharge was increased by 40 % due to improved power transfer efficient. However electron temperature became more non-uniform in MICP. Simulation results showed that density distribution of neutral species such as CF, CF_2, CF_3 were primarily affected by flow field. Highest density was observed on the top of electrode where the flow velocity was lowest.

PS-TuP6   Molecular Dynamics Simulation Study on Polymer Formation during Silicon Oxide (SiO_2) and Silicon Nitride (SiN) Etching by Fluoro/Hydrofluorocarbon Plasmas, *Satoshi Hamaguchi, M. Isobe, K. Miyake, K. Karahashi*, Osaka University, Japan, *M. Fukasawa, K. Nagahata, T. Tatsumi*, Sony Corporation, Japan
For the past several years we have been working on molecular dynamics (MD) simulation on silicon dioxide (SiO_2) and silicon nitride (SiN) etching by fluorocarbon (FC) or hydrofluorocarbon (HFC) ion beams such as CF_x^+ or $CF_xH_y^+$ in order to understand surface reactions and mechanisms of selective etching processes of SiO_2 and SiN by FC/HFC plasmas [1]. In our study, the sputtering yields and surface chemical compositions after etching obtained from MD simulations are compared with those obtained from beam experiments. Recently we have improved the predictive capability of our simulation code and successfully obtained sputtering yields from MD simulation that are in reasonable agreement with those observed in the corresponding beam experiments. In this presentation, we shall discuss what aspects of MD simulation techniques need to be most carefully designed in order for the simulator to reproduce realistic beam-surface interactions.

Selective etching of SiN over SiO_2 or vice versa is widely used in the microelectronics industry. It has been known that, at relatively low incident energy, FC or HFC ions such as CF_x^+ or $CF_xH_y^+$ incident upon a SiO_2 or SiN surface can etch the material surface while forming a thin polymer film on it. The thickness and chemical compositions of such a polymer film sensitively affect the etch rate (i.e., sputtering yield) of the material underneath. Therefore, for an MD simulation to represent beam-surface interactions with high accuracy, the simulation needs to correctly reproduce physical processes of polymer formation. It has been demonstrated that highly accurate carbon (C)-fluorine (F) interatomic potential models including electronegativity of F and an efficient thermostat algorithm to remove excess heat from incident ions are the key for better representation of ion-surface interactions by MD simulation.

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PS-TuP7   Development of a Compact Microwave Plasma Density Sensor for Processing Plasma Monitoring, *JinSheng Chiou, W.C. Chen, C.H. Hsieh, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China
Plasma density is a key parameter that control the property of processing plasmas and hence the processing results. It is thus of great interest to develop a sensor not only for characterization of the plasmas but also for monitoring of the plasma based processes1. In this study, a compact microwave plasma density probe was developed and the effect of plasma sheath and pre-sheath was also investigated. The principle of the probe is based on the resonant absorption of microwave of a coaxial antenna immersed in the plasma. In this study, the probe has a outer diameter 0.9 mm, designed to minimize the perturbation to the plasma. It consists of a monopole antenna formed by a short section of the center conductor of a semi-rigid coaxial cable and a glass enclosure. Experimental measurements were carried out in an inductively coupled plasma and the results show that the resonance frequency increase linearly with the source rf power, as expected. The results are also consistent with that from measurements by a Langmuir probe. The compact probe was also investigated numerically by employing a full wave electromagnetic simulation using a finite element code (COMSOL). In the simulation analysis, a coaxial line was attached to the probe head and the "driven mode" was adopted, i.e., the wave was fed into the coaxial line and the absorption spectrum, reflection coefficient vs frequency, was then analyzed. The plasma surrounding the probe was characterized by the collisional electromagnetic plasma permittivity, determined by plasma density, wave frequency and momentum transfer collisional frequency. The simulation results show that the absorption spectrum exhibits a resonance, occurring between the plasma frequency and the surface plasma wave resonance frequency [1]. The effect of plasma sheath and presheath was also studied by the numerical simulation where the sheath (floating) was modeled by an air gap of thickness twice the Debye length while a linear plasma density distribution was assumed for the presheath region. The resonance frequency was also found to be dependent of the probe diameter and antenna length. These results are consistent with the results obtained by experimental measurements. This indicates that one can use the result from numerical simulation as a calibration for the plasma resonance probe measurement.

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PS-TuP8   Impact of Magnetic Neutral-Loop Discharge Plasma on Low-k Dielectrics, *Weiyi Li, S-H. Kim, J. Blatz*, University of Wisconsin-Madison, *B.H. Moon, Y.M. Sung*, Kyungsung University (Korea), *S. Banna*, AMAT, *Y. Nishi*, Stanford University, *J.L. Shohet*, University of Wisconsin-Madison
The magnetic neutral-loop discharge (NLD) plasma was proposed by Uchida in 1994. We developed an NLD plasma reactor using a stainless-steel chamber, instead of commonly used quartz chamber in previous work. In order to examine the usefulness of this NLD reactor, low-k dielectric films are exposed to the NLD plasma under various conditions.

The structure of the NLD plasma reactor is described as follows. A cylindrical chamber lies in the middle of three sets of magnetic coils. With DC currents flowing in opposite direction in the middle set against side sets of coils, a circle on which magnetic field is zero, *i.e.* neutral loop(NL), can be produced in the middle of the chamber. In order to generate plasma, 13.56 MHz RF is inductively coupled into the chamber with a spiral antenna, through a quartz window on one end of the chamber. The reactor can be operated at two modes, NLD mode when there are opposite direction DC currents in the magnetic coils, or ICP mode when there are no DC

currents or same direction DC currents in the magnetic coils. In NLD mode, the plasma was observed to be brighter near the NL than in the center. This difference was further confirmed with a measurement of optical spectrum using an OceanOptics spectrometer, which shows the relative plasma glow brightness at the NL is as twice high as near the center of the chamber, and about 10% higher than a non-NLD ICP plasma.

By adjusting the ratio of the DC currents running in the magnetic coils, the position of the NL can be changed. Both experiment and simulation show that the glow follows the change of NL, especially at low pressure (<1 mTorr), due to much less collision.

Low-k dielectrics are widely used in modern back-end processing, in order to reduce the R-C delay in interconnection. During processing, low-k dielectrics are often subjected to plasma exposure. The consequent damage to low-k dielectric films is presented and compared with other types of plasma reactors.

PS-TuP9 Characterization and Simulation of a VHF Remote Plasma Source, *Scott Polak*, *D. Carter,* Advanced Energy Industries, *A. Bhoj, A. Roy,* ESI US R&D Inc.

This paper describes a novel, remote source technology using capacitively coupled, VHF energy to produce a flexible and unique plasma generator. The electrode design and internal construction are compatible with most processing chemistries, allowing generation of very low to very high plasma densities across extensive flow and pressure regimes. Furthermore, Langmuir and IEDF probe measurements have illustrated a competency of the remote source to deliver plasma well beyond the output of the apparatus, into large downstream chambers. This ability makes both neutral-radical and downstream ion enhanced processing possible. Due to the enhanced efficacy of this remote plasma source, optimization and characterization across the wide operating range becomes challenging. To facilitate characterization of the remote source and to augment empirical testing, plasma simulation techniques are employed. Commercially available, multi-physics code, CFD-ACE+, is used to simultaneously solve for the electromagnetics, fluid flow, heat transfer, species chemistry and transport equations for non-equilibrium discharges. A summary of the important remote source design elements will be reviewed along with a comparison of actual and simulated results, illustrating details of the plasma generation and distribution from this new technology.

PS-TuP10 Temporally and Spatially Resolved Optical Emission Spectroscopy of Capacitively Coupled Pulsed Plasmas, *John Poulose*, *L.J. Overzet, M.J. Goeckner*, University of Texas at Dallas

Pulsed plasma provides a method to 'independently' control ion and neutral fluxes. Temporal and spatial evolutions of the pulsed plasmas have been studied to provide a better understanding of transitory behavior in such systems. The optical emission intensities (OEIs) of various lines (atomic and molecular) from pulsed plasmas through Ar, O2, and N2 gases have been collected. The RF power was turned on and off at frequencies of 1, 10 and 100 kHz with a 50% duty cycle. The OEIs measured from argon plasma have shown a longer turn on/off time than those measured from O2 or N2 pulsed plasmas. Specifically, the OEIs measured from pulsed argon plasmas are still rising at the end of the on-time and do not completely extinguish at the end of the off-time at 100 kHz. This is in comparison to pulsed plasmas through both O2 and N2 in which the OEIs completely extinguish during the off-time and reach an apparent steady state level during the on-time. Additionally, the OEIs contract radially just after the start of the on-time for pulsed plasmas through argon, but a similar radial contraction phase is not found in the other gases. The radial extent of the OEIs in O2 and N2 remains essentially constant. We will present these results and the effects of other parameter and gases on the transitory behavior of pulsed discharges.

PS-TuP11 Laser-induced Incandescence Diagnostic for *In Situ* Monitoring of Synhtesis of Nanoparticles in Plasma, *James Mitrani*, *B. Stratton, Y. Raitses*, Princeton Plasma Physics Laboratory

A DC arc discharge with a consumed graphite, anode electrode is commonly used for synthesis of carbon nanoparticles, including buckyballs, nanofibers, and nanotubes [1-3]. The graphite electrode is vaporized, leading to nanoparticle synthesis in a low temperature (0.1 – 1 eV), atmospheric pressure plasma. The formation of nanoparticles in this plasma is poorly understood. For example, it is not clear where nanoparticles nucleate and grow in the arc discharge. To tackle this problem, a laser-induced incandescence (LII) diagnostic for in situ monitoring of the nanoparticles' spatial distribution in the plasma is currently being

constructed. The LII diagnostic involves heating the particles with a short-pulsed laser, and measuring the resulting spatial and temporal incandescence profiles on longer timescales [4]. By appropriately modeling the spatiotemporal incandescence profiles, one can measure the particle diameters and volume fraction. LII diagnostics have been extensively used to study soot particles in various backgrounds, including laboratory flames, smokestacks, and engines. However, LII has only recently been applied to study engineered nanoparticles, and has never been applied in a strongly coupled plasma background, such as a carbon arc discharge. Even though the spatial scale-lengths for soot and nanoparticles are similar (10-100 nm), great care is needed in developing an LII diagnostic for monitoring nanoparticles in an atmospheric pressure plasma. Therefore, we will initially calibrate our LII diagnostic by measuring spatiotemporal incandescence profiles of known, research grade carbon particles, including soot and nanoparticles. Preliminary results of this study will be discussed. [1] C. Journet et al. Nature 388, 756-8 (1997); [2] A. J. Fetterman et al. Carbon 46 1322-6 (2008); [3] M. Keidar et al. Phys. Plasmas 17, 057101 (2010); [4] C. Schultz et al. Appl. Phys B 83, 333-54 (2006).

PS-TuP12 Influence of Porosity on Electrical Properties of Low-k Dielectrics Irradiated with Vacuum Ultraviolet Radiation, *F.A. Choudhury,* University of Wisconsin-Madison, *J.-F. de Marneffe, M. Baklanov,* IMEC, KU Leuven Belgium, *Y. Nishi,* Stanford University, **Leon Shohet**, University of Wisconsin-Madison

During plasma processing, low-k dielectric films are exposed to high levels of vacuum ultraviolet (VUV) radiation emitted from the plasma. To reduce the dielectric constant of organosilicate (OSG) low-k materials, porosities (up to 50%) are introduced in the dielectric layer. The porous structure of these materials makes them even more sensitive to VUV modification due to their low density and deep penetration of photons into the film[1]. The effects of VUV photons on the chemical modification of OSG low-k materials as a function of porosity has been reported recently[1] and showed that OSG films having high porosities undergo higher $Si-CH_3$ depletion and severe chemical degradation. In this work, we investigate the changes to the electrical properties of porous low-k dielectrics as a function of porosity after VUV irradiation. VUV irradiation introduces defect states and generates trapped charges within the dielectric that can degrade the electrical properties of the film[2]. In order to investigate the influence of the porosity on the electrical properties after VUV exposure, organic low-k films of porosities between 15 and 50% were exposed to synchrotron VUV radiation of energies ranging from 6 to 15 eV and fluences up to 5×10^{14} photons/cm^2 to find the most damaging photon energies. CV measurements showed an increase in the dielectric constant along with a flat-band voltage shift and the presence of hysteresis after VUV irradiation. Initial IV and TDDB measurements indicate an increase in leakage currents along with lower breakdown fields after VUV irradiation. It is likely that these effects will be a function of VUV photon energy.[3]

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PS-TuP13 Ink Cap to Preserve Nanostructure during Sample Preparation for Electron Microscopy, *Brian Krist*, *J.S. Chawla, M. Chandhok, S.R. Cook, H.J. Yoo*, Intel Corporation

Transmission electron microscopy (TEM) imaging of narrow critical dimension (CD) features patterned in low-k materials is critical for functional validation of the patterning process steps. For interconnect applications in particular, low-k porous dielectrics can be mechanically weak and suffer structural damage from plasma processing due to higher carbon content.

Cross-section TEM sample lamellae prepared by focused ion beam (FIB) milling using conventional in-situ protective cap materials like insulator deposition (IDep, eg. TEOS), Pt, and W alter the low-k material line width, edge/surface roughness, and profile due to stress and high energy secondary electron interaction during localized capping. In addition, the conventional cap materials cannot gap fill features trenches that are less than 20 nm wide. Gapfill defects can cause poor mechanical stability during TEM sample

preparation and imaging. These defects can also lead to ion beam damage during TEM sample preparation.

In this paper, we investigate the ability of the ex-situ liquid inks as cap material for TEM cross-section sample lamellae to replace conventional in-situ cap materials. The use of ink fill protects the surface from the secondary electron beam damage that occurs using conventional in-situ FIB dual beam capping methods. Ink fill capped samples have undistorted ILD patterns that hold to zone axis. The ink to Pt FIB mill is matched unlike high dense high stress IDep so both sample thickness and stress are more consistent. Several inks where reviewed and down selected for lack of high aspect ratio fill, or inability to cure out solvents in ink. Cross-section images in this work use either hand dispensed *BIC Mark it,* or automate dispensed using *GenesisEcono-Jet* printer 3440BK INK.

We also demonstrate how ink fill capping enables imaging of the smallest features in interconnect process technology having low-k ILD.

PS-TuP15 Surface Modification to Improve Chemical Resistance of Coatings*, Gregory Peterson, W.O. Gordon,* Edgewood Chemical Biological Center*, E.M. Durke,* Excet, Inc.
Coatings are required to demonstrate chemical resistance in order to protect material, vehicles, and personnel. In addition, numerous other requirements for the development of new coatings often involve substantial reformulation efforts in order to adapt to changing conditions and applications. One method to improve chemical resistance of coatings is to modify the surface of the paint to reduce surface energy without changing the bulk; ensuring any bulk properties remain unaltered. Plasma-based chemical vapor deposition (PCVD) of perfluorinated compounds has been used for years to improve resistance of fabrics and materials to water and other chemicals. For example, there are several reports in the literature of superhydrophobic fabrics developed using PCVD. Here we report the application of a PCVD method that not only induces superhydrophobicity to a real world coating, but dramatically improves the resistance of the coating to the spreading and absorption of the chemical warfare agents, HD and VX. Over the 30 min age time, droplets remained pinned and are therefore more easily decontaminated or removed physically. Surface analysis confirms modification of the surface with fluorinated species and also shows etching of the organic components of the paint. This treatment suggests that surface modification strategies may be effective in improving chemical resistivity, without changing the bulk properties, or requiring a significant reformulation effort.

PS-TuP16 The Effect of Electron-Molecule Collision Cross Sections on Plasma Models*, Sebastian Mohr,* Quantemol Ltd, UK*, J.R. Hamilton, A. Asokan, J.C. Tennyson,* University College London, UK
Discharges in reactive gases such as SF6 and C4F8 are commonly used for industrial etching and deposition processes. The necessary surface reactions are induced by the free radicals in these discharges which are created by electron impact and heavy particle collisions. The process speed is thus usually determined by the densities of the free radicals, a prior knowledge of these densities and their dependence on parameters such as the pressure, input power or the gas composition is desired.

Numerical simulations of reactive gas discharges are employed to systematically study the chemical reaction rates and particle densities as functions of the aforementioned parameters. Furthermore, a reliable set of rate coefficients or cross sections for the included reactions are needed.

Quantemol-N, which provides full accessibility to the well-known UK molecular R-matrix codes [1], is used to model electron polyatomic molecule interactions including those with radicals. A wide range of cross-sections, otherwise not available experimentally are calculated for the required plasma chemistries. An expert system, Quantemol-VT, based on the Hybrid Plasma Equipment Model (HPEM) [2] is then used to model plasma tool on a reactor scale.

We provide results of a systematic study of an C4F8 discharge which is commonly used for deposition during the Bosch process. This study further compares the effect of including cross sections calculated with Quantemol-N against use of datasets comprising only known and commonly used cross sections taken from experimental studies. A plasma model of the discharge in a GEC cell is provided for a plasma chemistry containing CxFy radical reactions (calculated with Q-N) and without. The two models are compared and the role of CxF y radicals in plasma processing is highlighted.

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PS-TuP17 Development of Microwave-driven 1- and 2-Dimensional Microplasma Arrays and Tests of Atmospheric-Pressure Film Deposition*, Alan Hoskinson, H.C. Thejaswini, J. Hopwood,* Tufts University
Microwave-driven microplasmas allow for the generation of cold atmospheric-pressure plasmas at higher time-averaged electron densities ($\sim 10^{14}$ cm^{-3}) than most other techniques. These high densities may open unique regimes for high-pressure materials processing. The low ion energies (due to the short mean free paths at atmospheric pressure) may be partially compensated for by extremely large fluxes of ions and energetic metastable species while maintaining low gas temperatures. We present data from exploratory experiments showing rapid deposition of diamond-like carbon films at atmospheric pressure using a single microplasma. The development of one- and two-dimensional arrays of such microplasmas demonstrates a path towards film deposition on moderate-area substrates.

PS-TuP18 Mechanical Property of Polyurethane Nanocomposite Film with Carbon Nanotubes Functionalized by Atmospheric Dielectric Barrier Discharge*, D. Ogawa, Keiji Nakamura,* Chubu University, Japan
Polymers composited with carbonanotubes (CNTs) have been researched for many years to modify their material properties. This is because a polymer is mechanically soft and electrically insulated. The mix of CNTs is a good idea because CNTs can compensate the weakness of the polymer by making composites.

The functionalization of CNTs is a common technique for their applications due to chemical inertness of CNTs. This is why CNTs are generally difficult to disperse well in a liquid, while CNTs can disperse well after a functionalization. Nitric acid (HNO3) is commonly used to functionalize carboxyl group on CNTs. The functional group is modified to the functional group to fit one's application. It is reported that plasma can also functionalize CNTs without using the acid by making reactive species generated in plasma.[1]

We want to enhance the mechanical property of polyurethane (PU) film (approximately 100um thickness) through functionalized multi-wall CNTs (MWCNTs). In order to achieve our goal, we created a dielectric barrier discharge (DBD) above the CNTs that is located at the bottom of a quartz test tube. The discharge was created with the peak-to-peak voltage at 9 kV, the frequency at 10 kHz, and the discharge pressure at atmospheric pressure. Our process gas was made with a certain combination among argon, nitrogen, hydrogen, and oxygen gas depending on the functionalized group we want to attach on the CNTs. Here, Fourier transform infrared (FTIR) spectrometer was used to identify the functional groups attached by plasma discharge. After the plasma treatment, the CNTs were dispersed into a tetrahydrofuran (THF) solvent. The solvent is so versatile because the solvent is miscible to water and dissolvable even to non-polar solution. Some parts of the CNTs were dispersed in a THF solvent so that the concentration of the CNTs in the solvent was found from the transmission of the light at 600 nm. The PU film formed after drying out the mixture of the solvent and the PU solution over night.

In order to evaluate the strength of the PU film, the PU film was rubbed with a sand paper for hours. Here, we compared the wearing rate of the PU film that is defined by dividing the film thickness over the time when the PU film was completely rubbed out. The mechanically stronger the PU polymer is, the more wearing rate was observed.

In the presentation, we will show our recent progresses of the PU film that contains the CNTs functionalized with atmospheric DBD plasma .

[1] A. Felten, C. Bittencourt and J. Pireaux, Nanotechnology 17 (2006) 1954–1959

PS-TuP20 Development of a Low Cost and Portable Needle Type DBD Jet Operated under Atmospheric Pressure*, Chieh-Wen Chen, Y.J. Yang, C.C. Hsu,* National Taiwan University, Taiwan, Republic of China
A low cost and portable needle-type DBD jet operated under atmospheric pressure is developed. The plasma jet is comprised of an inner grounding electrode made of stainless steel rod, a quartz tube serving as the dielectric layer, and an outer powered ring electrode that is attached to the outer surface of the quartz tube. The quartz tube is 6-cm long with inner and outer diameters of 6 and 8 mm, respectively. A needle (25G) is attached to one side of the quartz tube that serves as the exit nozzle. This jet is powered by a low cost portable power that is commercially available (PVM 12, Information Unlimited, USA). Helium with a flow rate below 2 slm is used as the plasma gas. With this arrangement, a jet approximately 2 mm long can be extended out of the needle tip. The key features of this jet are (i) low

cost: less than USD$100 per system, (ii) portable, and (iii) equipped with a robust needle. Diagnostic studies of this plasma jet and using it for materials processing with a spatial resolution down to 1 mm will be presented.

PS-TuP21 Development of Low Cost and Flexible Microplasma Generation Devices Operated under Atmospheric Pressure, *Chih-Ming Wang, T.H. Lin, Y.J. Yang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Microplasmas are plasmas with geometric dimension less than 1 mm. Due to its miniature size, fabrication of microplasma generation devices frequently involves high cost materials and/or processes, such semi-conductor manufacturing processes. In this work, we present the development of two types of low-cost flexible microplasma generation devices: devices made on paper substrates and on flexible printed circuit board (PCB). The former is made of paper, conductive carbon paste, and tape, while the latter is fabricated using commercially available process that makes printed circuit board. We exam the stability of the discharge and the lifetime of the devices. When the paper-based device is assembled as a dielectric barrier discharge (DBD)-type device, stable array of discharges can be sustained for tens of minutes. When it is assembled as a micro-hollow cathode discharge (MHCD)-type system, no array of discharge can be obtained and the device lifetime is no longer than 3 min. For the PCB-based device, stable array of discharges can be sustained for longer than one hour. The use of the PCB-based device to perform gas conversion is also demonstrated. CO_2 decomposition forming CO and O_2 is chosen as the system to test. It is shown that the power efficiency above 7% can be obtained under selected conditions.

PS-TuP22 A Low Cost and Flexible Microplasma Generation Device to Create Hydrophobic/Hydrophilic Contrast on Nonflat Surfaces, *Yao-Jhen Yang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents a cost-effective (less than a quarter per device) and easy-to-fabricate dielectric-barrier-discharge-type (DBD-type) microplasma generation device for maskless surface patterning. This device was made of double-side copper laminate. A process to define circuit patterns on printed circuit board was utilized to define the electrodes required for the microplasma generation device. This device was then utilized for maskless surface patterning, either creating hydrophobic patterns on hydrophilic surfaces or hydrophilic patterns on hydrophobic surfaces. The former patterns were obtained by plasma polymerization of c-C_4F_8 precursor under He atmosphere to form fluorocarbon on designated regions on glass surfaces. The optical emission spectrum shows the CF_2 emission (250 nm-380 nm), suggesting the dissociation of precursor molecules. The FTIR spectrum of the deposited film shows strong CF_2 absorption peak at 1250 cm^{-1}. The contact angle of the film ranges from 102 to 105 degree. The hydrophilic patterns on hydrophobic surfaces were obtained by treating a fluorocarbon-coated surface using this plasma-generation device under ambient air. Non-flat surface patterning using this device will be demonstrated. (This work was supported by National Science Council of Taiwan, the Republic of China 101-2221-E-002-163-MY2)

PS-TuP23 Control of Plasma in Solution Using Bipolar Pulsed Voltage, *Fei-Hung Huang, C.Y. Chou, H.W. Chang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents control of plasmas in saline solution using bipolar pulsed DC power. It is known that plasma of such a type generates inside the gas-phase that composes of water vapor, oxygen, and hydrogen through joule heating and/or electrolysis. We use a 1-ms-wide positive pulse of 550 V to ignite the plasma. Prior to this positive pulse, a 10-ms-wide pre-pulse is applied to generate electrolytic gas. By changing polarity the pre-pulse, namely positive pre-pulse (mode++), negative pre-pulse (mode-+), or without the pre-pulse (mode0+), the gas composition can be tailored. Optical emission spectroscopy shows OH, H, and O emissions, which implies that the plasma generates hydroxyl, H, and O radicals. We used a chemical probe, disodium salt of terephthalic acid, to quantify the formation rate of OH radicals using photoluminescence spectroscopy. To assess how the power type influences the efficiency in organic degradation, acid orange 7 (AO7) was chosen as the model organic materials. AO7 decolorization was quantified using ultraviolet-visible adsorption spectroscopy. AO7 degradation kinetics was fitted using 1st order kinetics. It is shown that mode-+ has a higher AO7 degradation rate constant as well as higher OH radical formation rate.

PS-TuP24 The Effect of the Electrode Diameter on the Behavior of Plasmas in Saline Solution, *Shen-Chieh Lin, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

In this presentation, the effects of the electrode diameter on the discharge behavior of plasmas in saline solution are studied. The plasma is driven by a bi-polar DC pulse power source with an applied voltage up to 700V and a pulse width above 0.05 ms. The driving electrode is a platinum wire covered by a glass tube to precisely define the area exposed to the solution. Platinum wires of four different diameters, namely 0.1 mm, 0.3 mm, 0.5 mm, and 1 mm, were used. The grounding electrode is a bare platinum wire 0.5 mm in diameter and it is immersed in 0.1 M NaCl solution. Current and voltage probes are used to monitor the current and voltage waveforms across the electrode surface. A high speed camera is used to capture the bubble behavior and plasma appearance. An optical emission spectrometer is used to analyze plasma emission light. It is found that the breakdown voltage decreases with the electrode diameter. At a given applied voltage, the current peak value and the emission time delay upon the onset of the voltage pulse both increase with the electrode diameter, while the power density increases with the decrease in the electrode diameter.

PS-TuP25 Surface Treatment Using Portable Dielectric Barrier Discharge Device, *Yao-Yi Kuo, W.S. Zseng, C.M. Wang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

A portable dielectric barrier discharge device operated under one atmosphere is developed and the use of this device for surface treatment is performed. This device consists of a powered electrode made of a copper plate, a ground electrode made of stainless steel woven wire mesh, and a quartz plate 1 mm in thickness that serves as dielectric barrier between powered and ground electrode. This device is driven by a portable power source that is commercially available. This power source supplies voltages up to 20 kV with a frequency of 20-50 kHz. This plasma system is compact and low cost. Surface treatment under air, argon, and nitrogen atmosphere on PET, glass, and PTFE substrates to enhance hydrophilicity is performed. It is found that the water contact angle of the glass surface decreases from 40° to below 10° after treated using this device for 5 min operated in air and argon. For PET surface treatment under argon atmosphere, the contact angle decreases from 70° to 20° after 5 min of treatment. Due to its low cost and compact size, this portable DBD device shows great potential in various applications where portable devices are desired.

PS-TuP27 *RF Pulsing Technology on Commercial CCP(Capacitively Coupled Plasma) Dielectric Etcher and ICP(Inductively Coupled Plasma) Conductor Etcher.*, *Taeho Shin*, SEMES, Republic of Korea

RF pulsing technology in dry etcher had been developed about 20 years ago. But recently as the device node falls below 20nm (pitch size) many etch problems such as profile distortion, poor uniformity control, etc. become critical issue to be cleared. Many commercial dry etchers are currently introducing various pulsing technologies on their process chamber to overcome those process issues. They have claimed many process merits with RF pulsing. However one of the main problems in RF pulsing in mass production fabs lies in slower etch rate and unstable plasma. We also have developed RF pulsing technology on our CCP type dielectric etcher and ICP type conductor etcher. We have tested and optimized many different RF configurations such as RF frequencies pulsing, DC(Direct Current) pulsing and secondary electrode pulsing. One of tested configurations, we have found that secondary electrode DC pulsing with 3 different RF frequencies biased wafer electrode showing higher etch rate with improved mask selectivity as well as controlled bottom CD(critical dimension). Those results might be due to the fact that higher density plasma with higher ion energy is generated by enhanced electron energy distribution function(EEDF) and narrowed high energy ion density with DC pulsing.

PS-TuP28 Plasma Damage Characterization in Backbone Carbon Organosilicate Glass Low-k Films - with Backbone Chains (-Si-R-R-Si-) and (-Si-R-Si-), *Haseeb Kazi, R. James, S. Gaddam, J.A. Kelber*, University of North Texas

X-ray photoelectron spectroscopy (XPS) and FTIR data indicate that organosilicate glass (OSG) films with backbone carbon (-Si-$(CH_2)_x$-Si-) exhibit significantly enhanced resistance to carbon loss upon exposure to O_2 plasma, atomic oxygen (O(^3P)) and vacuum ultraviolet photons (VUV+O_2) at 10^{-4} Torr O_2 compared to films with terminal methyl groups (Si-CH_3). Two different low-k films with backbone structures (-Si-$(CH_2)_2$-Si-) and (-Si-CH_2-Si-) were investigated separately. Films incorporating backbone ethyl groups (-Si-$(CH_2)_2$-Si-) were deposited from 1,2 bis (triethoxysilyl) ethane (BTESE) precursor by ebeam or plasma cross-linking with achievable dielectric constant (k) ~3.00. XPS spectra for PECVD and ebeam cross-linked films are similar. The effects of (O(^3P)) on ebeam cross-linked film indicates negligible carbon loss or Si oxidation, combined with C-O bond formation, under conditions where OSG films with terminal methyl groups exhibit > 80% carbon loss within the surface region of the film. C-O bond formation is never observed for terminal CH_3 groups. Further, backbone carbon (-Si-$(CH_2)_2$-Si-) films exposed to VUV+O_2 exhibit self-limiting, minimal net carbon loss and formation of C-O bonds within the surface region. In separate experiments, low-k films with methylene bridging unit (-Si-CH_2-Si-) were investigated which contains a

mixture of (-Si-CH$_2$-Si-) and (-Si-CH$_3$) bonding environments in the final deposited film (k=2.55). Data indicate these backbone carbon (-Si-CH$_2$-Si-) films when exposed to O$_2$ plasma exhibit higher carbon removal rate for terminal groups (-Si-CH$_3$) whereas carbon in the linking chain (-Si-CH$_2$-Si-) undergo relatively slower removal rate, with Si-O, C-O bond formation. This indicates that O$_2$ plasma-induced Si-C bond rupture still occurs in the linking unit, but with a low probability of simultaneous rupture of both Si-C bonds required for abstraction of an in-line methylene bridging group. The data thus demonstrate that OSG films containing backbone carbon groups exhibit greatly reduced rates of carbon loss in the presence of O$_2$ plasma, atomic O or VUV+O$_2$ compared to films with terminal carbon groups due to fundamentally different patterns of Si-C bond scission. The results reported here demonstrate the potential for OSG films with backbone carbon to resist O$_2$ plasma damage.

PS-TuP29   A Continuous Plasma-Liquid Interface formed by a Laminar Flow Liquid Water Jet and Atmospheric-pressure Microplasma, *BrittanyPaige Bishop*, S. Ghosh, I. Morrison, D. Scherson, R. Akolkar, R.M. Sankaran, Case Western Reserve University

Reactions at the interface of a plasma and a liquid surface have recently become important for applications in wastewater treatment, materials synthesis, and therapy. These experiments are typically carried out between an atmospheric-pressure plasma jet and a static liquid surface (i.e. liquid bath or film). Here, we present a continuous plasma-liquid interface formed by an atmospheric-pressure microplasma and an open air, laminar flow liquid water jet.

A vertically falling water jet is formed in open air by pumping liquid water through a microcapillary. The stability of the water jet is explained by the Plateau-Rayleigh instability. At low flow rates, surface tension leads to the breakup of the jet into droplets. At high flow rates, the jet becomes turbulent and again breaks up. The water jet is found to be highly stable at intermediate flow rates where the water jet is laminar, with a relatively constant diameter of 500 μm over lengths of more than 30 mm. This allows the microplasma to be stably formed at the surface of the water jet and current to flow across the plasma-liquid interface to a counter electrode. The system is characterized with the microplasma operating by current-voltage measurements. We find that the overall resistance is strongly influenced by the inter-electrode distance and the ion concentration in solution, suggesting that solution conductivity dominates the electrical conductivity of our system. This is explained by a simple model based on a geometrical approximation for the water jet which shows that the resistance of the water jet is large because of the confined volume.

We have applied this newly developed system to the synthesis of metal nanoparticles. Aqueous solutions of silver nitrate are formed as a liquid water jet and pumped through the plasma-liquid interface. A distinct color change is observed as the silver nitrate is reduced by the microplasma to silver nanoparticles. The solutions are characterized by ultraviolet-visible (UV-vis) absorbance spectroscopy and transmission electron microscopy (TEM) which confirm crystalline, nanometer-sized silver particles. We find that the particle production rate depends on the plasma current and the liquid water jet flow rate, the latter of which is consistent with a space time approximation for the reactor.

PS-TuP30   Anomalous Electron Cross-Field Transport in a Low Pressure Magnetized Plasma For Material Processing Applications, *Yevgeny Raitses*, Princeton Plasma Physics Laboratory

The application of the magnetic field in a low pressure plasma can cause a spatial separation of cold and hot electron groups. This so-called magnetic filter effect is used for many plasma applications, including ion and neutral beam sources, plasma processing of semiconductors and nanomaterials, and plasma thrusters. In spite of successful practical applications, the magnetic filter effect is not well understood. In this work, we explore this effect by characterizing the electron and ion energy distribution functions in a plasma column with crossed electric and magnetic fields. Experimental results revealed a strong dependence of spatial variations of the plasma properties across the magnetic field on the gas pressure. In particular, the results showed the existence of the gas pressure threshold below which the increase of the magnetic field leads to a more uniform profile of the electron temperature. This surprising result is due to anomalously high electron cross-field transport that causes mixing of hot and cold electrons. For xenon and argon gases, this threshold is ~ 1 motrr. At higher gas pressures, a stronger separation of cold and hot electrons, which is favorable for the above applications, was observed.

Wednesday Morning, November 12, 2014

Plasma Science and Technology
Room: 305 - Session PS1-WeM

Plasma Based Ion Implantation and Ion-Surface Interactions
Moderator: Aseem K. Srivastava, Applied Materials, Inc.

8:00am PS1-WeM1 Dosimetry Challenges for Plasma Doping and Ion Implantation, *Bo Vanderberg*, *L.M. Rubin, A.M. Ray*, Axcelis Technologies, Inc. **INVITED**
Plasma doping been described as a fledgling technology to complement and replace ion beam based implantation, due to its advantage in productivity given by the much higher average ion current delivered to work pieces. While productivity is an important factor in industrial applications, each technology also has to deliver appropriate dose control, and thus relies on advanced dosimetry systems to provide accurate dosage, high dose uniformity across the work piece, precise ion placement, i.e. energy and angle control, low contamination of undesired energetic and environmental species, and reliability and exception handling capability.

For commercial semiconductor manufacturing applications in particular, simultaneous compliance to each of these requirements is critical. Modern ion beam based implantation systems can provide dosimetry to meet these requirements, and we will describe some of the new technologies developed specifically for ion implantation of the most advanced semiconductor devices: fast data acquisition of multiple Faraday systems with parallel current collection, and measurement of spatial ion beam properties such energy and two-dimensional spatial and angle distribution, as well as their time dependence to monitor drift and intermittent failures.

For plasma doping to meet these standards, obstacles in terms of lack of mass-resolution, simultaneous implantation, deposition and etching, and lack of in situ beam monitoring during the plasma doping process represent formidable challenges. While some if the inherent shortcomings of plasma doping are fundamental, some techniques have been developed to address these issues, including novel Faraday systems as well as model based dosimetry with either theoretical or empirical modeling of plasma physical and chemical processes, some of which we will review.

The most difficult challenge for plasma doping is matching of dopant depth profiles of existing ion beam based implantation, where implanted dopant profiles as presented in the literature are different from their equivalent ion beam produced profiles. Without this capability, plasma doping of semiconductors is confined to a niche application space, covering less sensitive doping processes in semiconductor manufacture.

8:40am PS1-WeM3 Ion Implantation Challenges and Applications for Future Memory Devices, *Allen McTeer*, Micron Technology **INVITED**
For many years memory manufacturers resisted the need to adopt implant steps that were considered mainstream in logic manufacturing in order to keep cost down. In the last few years this approach has had to change to address scaling issues. Pre-amorphization, carbon, germanium and indium implants have been adopted by most memory manufacturers for dopant profile and silicide growth control. At the same time, plasma doping was adopted to address productivity issues seen with high dose, low energy beamline implants. These changes reflect the realization that technology challenges and cost mitigation are becoming more divergent with shrinking geometries. The introduction of emerging and vertical memory devices is expanding the applications of both beamline and plasma doping techniques. This talk will discuss some of the new implant applications that could be introduced in upcoming memory devices to address process needs. This will include discussion and data review of applications related to stress control, implant damage, silicon cracking, high aspect ratio implants, hydrogenation, surface modification, dopant profile control and interface cleaning.

9:20am PS1-WeM5 Challenges in Ion Implantation, *Joseph Olson*, *S. Chennadi, G. Gammel, N. Pradhan, F. Sinclair, S. Todorov, M. Welsch, R. White*, Applied Materials, Varian Semiconductor Equipment **INVITED**
Requirements on commercial ion implantation equipment grow increasingly stringent as device nodes progress. In the face of these tightening requirements the implanter designer is faced with the challenge of designing and building apparatus to measure and control process properties and then to validate improved performance. Recent examples of this process in action are discussed. (1) Precise control of the incidence angles of ions on a substrate is required for accurate placement of dopant atoms. Development to meet this need lead to advanced measurement and control systems and a powerful new technique (the 2D V curve) that produces a map of incident angles over an entire 300 mm Si substrate. The 2D V curve is explained in detail. (2) The current density in beamline implantation has potential process consequences on microuniformity, substrate charging and amorphization. The development of a beam density measurement, beam size control system and validation by examination of implanted wafers is discussed.

11:00am PS1-WeM10 Plasma Doping Process Monitoring Diagnostics, *Yuuki Kobayashi*, Tokyo Electron Limited, Japan, *P. Ventzek*, Tokyo Electron America, Inc., *K. Yamashita, S. Nishijima, M. Oka, H. Ueda, Y. Sugimoto, M. Horigome, T. Nozawa*, Tokyo Electron Limited, Japan
Plasma doping is an emerging technology for the doping of next generation topographic structures such as Fin-FET extensions. Typically a dopant precursor such as arsine in injected into a plasma source where the dopants are freed from the precursor and injected into a surface that is initially amorphized by the ion flux incident on the topographic structure. As the doping process is impacted by the precursor, ion and energy flux to the substrate, it is important to have diagnostics to measure these quantities. Knowing the dose as a function of the critical measureable plasma parameters allows a model to be developed for dose monitoring and control. The model need not be physically based but could also be statistical. The challenge is coming up with simple enough diagnostics that integrate in a non-contaminating way with the plasma. Independent measurement of plasma parameters is also important as a monitor of plasma source and process stability which also impact dose. We have developed a hybrid sensor set comprising of an in-situ current and optical emission (OES) monitors that are used to correlate with dose measurements corresponding to a radial line slot antenna plasma doping process. The in-situ current monitor enables measurement of plasma density and OES provides measurement of dopant radicals. Both monitoring methods, when used together, permit detection of previously immeasurable process drift affecting doping performance. In this presentation, we describe the sensors and typical results. The relationship between dose, plasma and optical measurements is discussed in terms of a descriptive model. A physical interpretation of the results is aided by simulations of the plasma for which we present summary results.

11:20am PS1-WeM11 Control over the Ion Flux Obtained by Sawtooth-like Waveforms in Radiofrequency Capacitively Coupled Plasmas, *Bastien Bruneau**, *T. Novikova, T. Lafleur, J.-P. Booth, E.V. Johnson*, Ecole Polytechnique, France
The use of Tailored Voltage Waveforms (TVWs) to manipulate the Electrical Asymmetry Effect (EAE) in a capacitively coupled plasma (CCP) chamber has been shown to be an effective technique for varying ion bombardment energy (IBE) at the surface of an electrode. It stems mainly from an amplitude asymmetry, i.e. from waveforms with different maximum and minimum. We present herein a new plasma asymmetry, obtained by sawtooth-like waveforms.

We use Particle-in-Cell (PIC) simulations to study an argon plasma excited by sawtooth-like waveforms. Using a waveform with slow rise and fast fall, we show that a fast fall leads to fast sheath expansion in front of the powered electrode, and therefore high ionization at this sheath edge. On the other hand, the slow fall leads to slow sheath expansion in front of the grounded electrode, and therefore to weak ionization at this sheath edge. This ionization asymmetry subsequently leads to an ion flux asymmetry, with up to twice higher flux on powered electrode. Because of this ion flux asymmetry, a positive self-bias develops in this plasma, leading to smaller IBE on the powered electrode compared to the grounded electrode. Therefore, the high-flux electrode also corresponds to the low-energy electrode. This property is unique, as it cannot be obtained with any of the geometrical asymmetry, amplitude asymmetry or with any mono-frequency RF excitation. We show that the ion flux asymmetry effect increases both with the number of frequencies composing the waveform, as the slope-asymmetry of the waveform then increases, and with pressure, as diffusion from one electrode to the other is hindered at high pressure. Waveforms optimizing the slope-asymmetry effect and allowing a fine and continuous control over the asymmetry are presented.

This slope asymmetry effect can be of great interest for any process using RF-CCP plasma, as one can control independently the ion flux on each electrode. For instance, one can imagine using a sawtooth-like waveform in a deposition (or etching) process. The deposition (or etching) rate can then be increased on the substrate of interest, while benefitting from a low IBE, and while keeping the up-time of the reactor high by keeping the

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* Coburn & Winters Student Award Finalist

maintenance-time low, thanks to the low deposition (or etching) rate on the other electrode.

11:40am PS1-WeM12 Surface Roughening Mechanisms and Roughness Suppression during Si Etching in Inductively Coupled Cl₂ Plasmas, *Nobuya Nakazaki*, *H. Matsumoto, K. Eriguchi, K. Ono*, Kyoto University, Japan

As ULSI device dimensions continue to be scaled down to << 100 nm, increasingly strict requirements are being imposed on plasma etching technology. The requirements include the precise control of profile, critical dimension, roughness, and their microscopic uniformity (or aspect-ration dependence), together with that of etch rate, selectivity, and damage. Atomic- or nanometer-scale surface roughness has become an important issue to be resolved in the fabrication of nanoscale devices, because the roughness at the feature bottom affects the uniformity of bottom surfaces, which in turn leads to a recess and thus a damage to transistors in gate fabrication. Moreover, the roughness on feature sidewalls is responsible for the line edge roughness (LER) and linewidth roughness (LWR), which affect the variability for gate or channel lengths and thus the variability in transistor performance. The formation of such surface roughness is stochastic and three dimensional, which are assumed to be affected by a number of factors during processing including plasma etching.

Experimental investigations of the surface roughness of planer substrate of Si etched in inductively coupled Cl₂ plasmas have been performed, including several surface and plasma diagnostics, to gain a deeper understanding the mechanisms for surface roughening and then to find a way for suppressing the roughness during plasma etching. The experiments indicated that as the rf bias power or incident ion energy E_i is increased, the etch rate continues to increase, while the surface roughness increases and then substantially decreases at high E_i. In addition, the surface roughness at low E_i increases with etching time, while does not depend on etching time at high E_i. The analysis of the etch rate as a function of E_i and etching time, with the help of Fourier transform infrared (FTIR) absorption spectroscopy, quadrupole mass spectrometry (QMS), and classical molecular dynamics (MD) simulation, implied that by-product ions of silicon chlorides $SiCl_x^+$, whose concentration is increased in the plasma at increased E_i, play a critical role in surface roughening as well as etching at increased E_i through competitive etching and deposition. [1,2] Moreover, the pulse-bias etching through a repetitive on/off of the rf bias power also have been demonstrated to be one promising way of reducing the surface roughness during plasma etching.

[1] H. Tsuda, N. Nakazaki, Y. Takao, K, Eriguchi, and K. Ono: J. Vac. Sci. Technol. B (2014) in press.

[2] N. Nakazaki, Y. Takao, K, Eriguchi, and K. Ono: Jpn. J. Appl. Phys. **53** (2014) 056201.

12:00pm PS1-WeM13 Ion Induced Electron Emission from Semiconductors: An Investigation into Fermi Level and Surface Electric Field Effects, *David Urrabazo*, *M.J. Goeckner, L.J. Overzet*, University of Texas at Dallas

A few recent publications point to the possibility of controlling the ion induced electron emission (IIEE) yield from semiconductor surfaces in real time through controlling the numbers of electrons in the semiconductor's conduction band ($n_{e,CB}$). Of course, ion bombardment induced electron emission also occurs in the plasma processing of semiconductors, and should cause differences between processing n- and p-type wafers if it truly depends upon $n_{e,CB}$. Hagstrum's Auger neutralization theory for semiconductors[1] assumes that the IIEE yield should NOT depend upon $n_{e,CB}$, and as a result most models make the assumption that the IIEE yield is independent of $n_{e,CB}$ (and the position of the Fermi level as well as temperature). To our knowledge, no one has investigated this assumption! Therefore, we have experimentally and theoretically investigated it by using and extending Hagstrum's theory as well as by measuring the IIEE yield from semiconductor samples versus doping density and type. Our results for Si demonstrate good agreement with the assumption both theoretically and experimentally. The IIEE yields of p-type, intrinsic and n-type samples are essentially the same. In direct contradiction to the theory/assumption, however; the IIEE yield for p-type Ge was measured to be 2.5 times greater than that of intrinsic and n-type samples. Precisely the opposite of what one might first expect! This result indicates that there can be other significant factors controlling the IIEE yield. One likely factor is a surface electric field. (It could have been induced by Fermi level pinning in the case of our Ge measurements, and in plasmas it could be induced by the sheath.) As a result, the new principle question becomes: Can a moderate surface electric field control the IIEE yield from semiconductors? To our knowledge, there are no unambiguous measurements answering this question either . Therefore, we will introduce a device we have designed, modeled, and begun fabricating for measuring the IIEE yield while allowing independent

control over the ion flux to the surface and electric field imposed on that surface.

[1]H.D. Hagstrum, Phys. Rev. 122 83 (1961)

Plasma Science and Technology
Room: 308 - Session PS2-WeM

Plasma Modeling
Moderator: Steven Shannon, North Carolina State University

8:00am PS2-WeM1 Self-Consistent Modeling of Capacitive Coupling in Inductively Coupled Plasmas, *Ankur Agarwal*, *S. Rauf, K. Collins*, Applied Materials Inc.

Plasma etching of microelectronic structures at advanced technological nodes (< 1x nm) places great emphasis on process uniformity.[1] Antenna designs have become more complicated in industrial inductively coupled plasma (ICP) tools to improve uniformity.[2] The antenna region in ICPs also contain auxiliary systems for gas flow, temperature control, etc. which influence the antenna electrical characteristics. Plasma equipment models typically employed to investigate ICP sources have used a circuit model to compute voltage and current along the coils to capture the antenna-plasma coupling self-consistently.[3,4] However, the approach is limited to simple coil structures which is not necessarily the case for next-generation ICP tools. For example, Applied Materials' AdvantEdge chamber utilizes a two-coil structure fed through the same power supply.[5]

In this work, we discuss results from a two-dimensional plasma equipment model, HPEM[6], which has been modified to compute the voltage and current (amplitude and phase) in the coils by solving the equivalent circuit of the coils and the plasma in the frequency domain. The plasma is treated as the secondary coil of an air-core transformer. The amplitude of the driving voltage is adjusted in the circuit model such that the sum of inductive, capacitive and resistive powers is maintained constant. Capacitive coupling is calculated by including the voltage on the coils in the Poisson's equation. The coil currents from the circuit model are used as driving terms in the solution of the wave equation and to compute resistive losses in the coils.

Results will be discussed for an Ar/Cl₂ plasma and the consequences of varying electronegativity of the feedstock gas mixture, varying current ratios between the two-coils and the phase of current between the coils on capacitive coupling will be assessed over a pressure range of 5 – 150 mTorr. We found that inductive component of the power coupled increases with pressure from 5 to 30 mTorr as the increase in electron density supersedes the rise in collision frequency. While, power is dominantly coupled inductively for electropositive gas mixture, the pressure at which transition to capacitive mode occurs decreases as electronegativity increases.

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

[2] Ch. Hollenstein, et al., Plasma Sources Sci. Technol. **22**, 055021 (2013).

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8:20am PS2-WeM2 Experimentally Guided Development of a Dielectric Etch Plasma Model, *Ajit Balakrishna*, *S. Rauf, K. Collins*, Applied Materials Inc.

Smaller technology nodes in the semiconductor industry place increased emphasis on etch productivity requirements, such as etch rate and critical dimension. Modeling and simulation play a central role in new developments (design of new hardware and exploration of novel processing options) to address the concurrent demand for improved performance and shorter development cycle. Validation against experimental data is a critical step in making these models a mature development tool. In this study, we have developed, refined and validated a dielectric etch process model based on blanket wafer etching results.

In an earlier study, we tested a 2-dimensional model for capacitively coupled plasmas (CCP) in combination with a surface mechanism model against experimental data for etching of blanket SiO₂ wafers in a dual-frequency CCP plasma etcher. The process parameters for this c-C₄F₈/O₂/Ar plasma were varied over a wide range of pressures (25-150 mTorr), bias

powers (500-1500 W), and c-C_4F_8 and O_2 flows. The etch rate increased with bias power and c-C_4F_8 flow rate, weakly decreased with increasing O_2 flow rate, and moderately increased with pressure. The reactor simulations were performed using CRTRS, a 2/3-dimensional fluid plasma model. The plasma simulations provided fluxes of various fluorocarbon polymerizing species, atomic oxygen and atomic fluorine. We also calculated fluxes and energies of the ions impacting the wafer. Based on comparisons to the experimental data, we selected a coverage based etch mechanism. This mechanism described center-point etch rates well but indicated that the model needed some improvements to predict the radial etch rate profile and to capture the sensitivity to pressure.

Closer examination of the fluid plasma modeling results revealed that the electron density, and consequently the etch reactants, peaked near the wafer edge. The experimental profiles, on the other hand, showed a slight center-high profile. In the fluid plasma model, the electrons absorbed power at the wafer edge and increased reaction rates close to this power-absorption region. At lower pressures (with fewer collisions), this model was not capturing the non-local behavior of high-energy electrons. A Monte Carlo model provided better spatial representation of electron kinetics and this was coupled with the fluid plasma model. This hybrid plasma model significantly improved the experimental match. Both coverage and thickness based dielectric etching mechanisms were tested. In addition to these improvements, careful accounting for the power going into DC and RF modes gave greater model fidelity to the observed pressure sensitivity.

8:40am **PS2-WeM3 Insights to Critical Dimension Control Through 3-Dimensional Profile Simulation For Plasma Etching**, *Yiting Zhang**, *M.J. Kushner,* University of Michigan*, S. Sriraman, A. Paterson*, Lam Research Corp

Plasma assisted etching is a necessary process for pattern transfer in microelectronics fabrication. In prior technology nodes, 2-dimensional feature profile models served very well to help optimize features and connect reactor scale properties to feature scale critical dimensions (CDs). The current technology nodes utilize 3-dimensional structures such as FinFETs and Tri-Gate transistors, whose optimization is considerably more difficult and not well represented by 2D profile simulators. For example, etching of 3D structures typically require longer over-etch to clear corners, which then places additional challenges on selectivity to maintain CD. Prior CD control techniques are evolving to address these issues.

In this paper, we report on development of a 3-dimensional profile simulator, the Monte Carlo Feature Profile Model (MCFPM-3D). The MCFPM-3D builds upon the 2D MCFPM modeling platform that has many advanced features such as charging, mixing, implantation and photon stimulated processes. The same reaction mechanism used for the 2D model can be used in MCFPM-3D. The MCFPM-3D uses a rectilinear mesh in 3 dimensions having fine enough resolution that, for example, circular vias can be resolved. Each cell within the mesh may represent a different solid material or a mixture of materials. The model addresses reaction mechanisms resulting in etching, sputtering, mixing and deposition on the surface to predict profile evolution based on fluxes of radical, ions and photons provided by an equipment scale simulator. In these studies, energy and angularly resolved fluxes are provided by the Hybrid Plasma Equipment Model (HPEM).

To address evolving CD control issues, results from the model will be used to compare etching of 2D and 3D structures. Ar/Cl_2 and $Ar/CF_4/O_2$ plasmas are used for Si and SiO_2 etching in representative 2D and 3D feature topographies relevant to etch applications in advanced technology nodes. Phenomena such as line-edge roughness, reactive ion etch lag and aspect ratio dependent etching will be discussed.

9:00am **PS2-WeM4 3-Dimensional Model for Electron-Beam Generated Plasma**, *Shahid Rauf, A. Balakrishna, A. Agarwal, J. Kenney, L. Dorf, K. Collins*, Applied Materials Inc.

Plasmas generated using energetic electron beams have unique properties that make them attractive for emerging plasma processing applications. In the pioneering work done at the Naval Research Laboratory, [1] it has been demonstrated that electron temperature (T_e) in the electron-beam generated plasmas is typically < 0.8 eV while electron densities are comparable to those obtained in radio-frequency (RF) inductively and capacitively coupled plasmas. In addition, the ions and radicals are primarily produced by highly energetic electrons (few keV) instead of electrons in the tail of a low energy distribution. The plasma chemistry in electron-beam generated plasmas is therefore significantly different to RF plasmas with a much higher ion to neutral radical density ratio. As feature dimensions shrink below 20 nm in microelectronics devices with atomic level precision required during manufacturing, the unique properties of electron-beam generated plasmas

(low T_e, low ion energy and unique chemistry) are increasingly becoming attractive for plasma processing in the semiconductor industry.

For typical gas pressures used in electron beam generated plasmas (– 50 mTorr), self-induced electric field and collisions can quickly broaden the electron beam. A relatively strong magnetic field parallel to the beam direction has therefore been employed to confine the electron beam. [1] Many complex mechanisms effect uniformity of a magnetized plasma, especially if the magnetic field is inhomogeneous and near the edges of the plasma. We have developed a 3-dimensional plasma model to better understand the spatial characteristics of electron-beam generated magnetized plasmas. The bulk plasma electrons are treated as a fluid and the model includes continuity equations for charged and neutral species, momentum equation for ions, and energy conservation equation for electrons. A Monte Carlo model is used for electron beam transport through the vacuum and plasma regions, which includes gas phase collisions and the effect of magnetic field and electric fields on electron motion.

The 3-dimensional plasma model is used to understand the spatial characteristics of electron beam generated Ar, N_2 and O_2 plasmas. These simulations have been done for a plasma chamber with radius < 30 cm, and several magnet designs. The impact of magnetic field, beam electron energy, and gas pressure on uniformity of important plasma properties (electron and ion densities, radical densities, T_e) is examined. Modeling results are also validated against probe measurements. [1]

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9:20am **PS2-WeM5 From Nonlocal Electron Kinetic Theory to Practical Applications**, *Igor Kaganovich*, Princeton Plasma Physics Laboratory*, D. Sydorenko,* University of Alberta, Canada*, A. Khrabrov, Y. Raitses,* Princeton Plasma Physics Laboratory*, P. Ventzek, L. Chen*, Tokyo Electron America, Inc.

The purpose of the talk is to describe recent advances in nonlocal electron kinetics in low-pressure plasmas. Partially-ionized, bounded, and weakly-collisional plasmas demonstrate nonlocal electron kinetic effects, nonlinear processes in the sheaths, beam-plasma interaction, collisionless electron heating, etc. Recently Physics of Plasmas published special topic of collected papers dedicated to "Electron kinetic effects in low temperature plasmas" in memory of the pioneer and leader of this field, Professor Lev D. Tsendin [1]. The plethora of kinetic processes supporting the non-equilibrium plasma state is an invaluable tool, which can be used to adjust plasma parameters to the specific needs of a particular plasma application. We report on recent advances in nonlocal electron kinetics in low-pressure plasmas where a non-Maxwellian electron velocity distribution function was "designed" for a specific application: in dc discharges with auxiliary biased electrodes for plasma control [2], hybrid DC/RF unmagnetized [3] and magnetized plasma sources [4], and Hall thruster discharges [5]. We show using specific examples that this progress was made possible by synergy between full-scale particle-in-cell simulations, analytical models, and experiments. Initial "academic" studies paved the way to understanding of modern plasma devices that are being developed for future plasma technology. One example is so-called non-ambipolar electron plasma, where an electron beam is extracted through a small aperture [6]. Our previous studies of extraction system [2] and collective interaction of electron beam with the plasma aides understanding and optimization of this device [6]. Another example is modeling of high power plasma switch for electric grid system [7].

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9:40am **PS2-WeM6 Electromagnetic Modeling of Inductively-Coupled Plasma Sources with Realistic Plasma Loads**, *Jason Kenney, S. Rauf, K. Collins*, Applied Materials, Inc.

Design of inductively-coupled plasma (ICP) sources for industrial tools is a challenging process, often relying on multiple classes of models owing to differing design goals and model limitations. A basic progression may

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* Coburn & Winters Student Award Finalist

include two-dimensional (2D) plasma modeling to fix the source architecture; three-dimensional (3D) electromagnetic (EM) modeling to investigate feed structures, current requirements, and azimuthal uniformity; and thermal modeling of source components using heat loads from the plasma and EM modeling. For the 2D plasma simulation, a typical approach assumes that power is coupled into the plasma volume purely inductively [1], reducing the source calculation to computation of azimuthal electric fields arising from coil currents. This can be enhanced by modifying the equivalent circuit of coils and plasma to account for capacitive and resistive powers.[2]

The computational expense of a coupled 3D plasma and EM model—which would require a fine mesh to capture source details along with a large number of computational cycles to allow the plasma properties to reach steady-state—is generally avoided through appropriate assumptions. In the 3D EM model, the simplest assumption is to represent the plasma as a conductive medium with conductivity matching that of a plasma with assumed density (or density profile) similar to the plasma simulation. However, in this work, we consider the impact of a more realistic treatment of a plasma load in a 3D finite-element time-domain (FDTD) EM model. In this method, the Maxwell Equations are solved in a leapfrog manner, updating electric and magnetic field vectors in turn. Rather than assume the plasma is a fixed medium with assumed conductivity, we consider the plasma current through solving the linearized momentum conservation equation for electrons, which is coupled to the Maxwell equations. It is assumed that ions are fixed. In addition, we consider methods to capture the nonlinear sheath dynamics by treating the sheath as a nonlinear circuit element and embedding these elements at the plasma – material interfaces in the mesh.

Discussion will be focused on impact of ICP source frequency and power for low pressure conditions (~20 mT) typical of ICP operation.

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11:00am PS2-WeM10 Two Dimensional Simulations of the Impact of Weak Magnetic Fields on the Plasma Properties of a Planar Slot Antenna Surface Wave Driven Plasma Source, *Jun Yoshikawa*, Tokyo Electron Ltd.*, Y. Susa,* Tokyo Electron Miyagi Limited*, P. Ventzek*, Tokyo Electron America, Inc.

The radial line slot antenna plasma source is a type of surface wave plasma source driven by a planar slotted antenna. Microwave power is transmitted through a slot antenna structure and dielectric 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 renders the source useful for soft etch applications and thin film deposition processes requiring low ion energy. Another property of the diffusion zone is that the plasma density tends to decrease from the axis to the walls under the action of ambipolar diffusion. A previous simulation study [1] predicted that the anisotropy in transport parameters due to weak static magnetic fields less than 50 Gauss could be leveraged to manipulate the plasma profile in the radical direction. These simulations motivated experimental tests in which weak magnetic fields were applied to a radial line slot antenna source. Plasma absorption probe measurements of electron density and etch rate measurements showed that the magnetic fields remote from the wafer were able to manipulate both electron density and etch rate. The presentation includes a brief recap of the first simulations, a summary of the experimental results and new simulation results that mate to these experiments. [1] J. Vac. Sci. Technol. A 31, 031306 (2013)

11:20am PS2-WeM11 Analytical Model of Plasma Sheaths at Intermediate Radio Frequencies, *Mark Sobolewski*, NIST

Analytical models of plasma sheaths provide physical insight and are useful in 2-d and 3-d plasma simulations, where numerical solution of the sheath equations at each boundary point is too time-consuming to be practical. Analytical models have long been known for the high-frequency and low-frequency limits, where the time it takes ions to cross the sheath, t_i, is either much greater than or much less than the rf period, T. At intermediate frequencies, where $t_i \approx T$, sheath behavior is more complicated. In addition to the well-known narrowing of ion energy distributions (IEDs) there are other, lesser known effects at $t_i \approx T$, including changes in the ion current — which becomes strongly time-dependent within the sheath — and in IED peak intensities, average ion energy, sheath impedance, and sheath power. Existing analytical models of collisionless sheaths based on the "damped potential" formalism yield accurate predictions for IED widths and peak energies, but not for any of the other phenomena. Here, we describe a different approach for modeling intermediate-frequency, collisionless sheaths. It captures the essential elements of ion dynamics yet still provides analytical expressions for most sheath properties. Others require minimal numerical effort, such as a single numerical integration of an analytical

expression. Predictions of the analytical model are compared to previous analytical results, complete numerical solutions of the relevant partial differential equations, and, where possible, experimental data. The model yields new insights into ion dynamics and may serve to increase the accuracy of 2-d and 3-d plasma simulations, in particular, their predictions for power and average ion energy.

11:40am PS2-WeM12 Plasma Prize Invited Lecture: Simulations of Plasma Processes and Equipment for Semiconductor Device Fabrication, *Peter Ventzek*, Tokyo Electron America, Inc. **INVITED**

For decades, simulation and theory has been applied to the design and analysis of semiconductor process and fabrication equipment development. Simulation technology has advanced from predictions of the electron energy distribution function and plasma chemistry to multidimensional simulations of plasma equipment. Multidimensional plasma source models have been used to predict (and sometimes post-predict) many important phenomena. Prediction of the consequence of augmentation of sources with weak magnetic fields is used to illustrate this. Progress in surface topography evolution models and sub-surface property prediction has been similarly impressive. Complemented with classical force field molecular dynamics simulations have been used to address critical problems related to patterning and atomic layer etching. While fully integrated equipment-feature scale models have been demonstrated, they remain less than tightly coupled because of difficulties dealing with plasma and plasma-surface chemistry. While this presentation will not reveal closing of gaps between models, progress in coupling can be reported. Advances in quantum chemistry and molecular dynamics methods permit insights to be gained from existing simulations of plasma sources. We will use the example of plasma doping using microwave plasma sources as an example. Techniques that complement equipment simulations such as highly resolved particle-in-cell simulations and test particle methods help reveal how the physics of the plasma source is related to phenomena at the surface and sub-surface. Once akin to "Imagineering," Modeling and simulation is now pervasive in the semiconductor industry. Globally this is manifested through direct activity in industry or through interactions with consortia or academia. The presentation will provide a perspective on future directions in the field.

Thin Film
Room: 307 - Session TF+MS+PS-WeM

Applied ALD: Nanoelectronics and Emerging Applications
Moderator: Jesse Jur, North Carolina State University

8:00am TF+MS+PS-WeM1 ALD and Beyond CMOS Materials, *Robert Wallace*, University of Texas at Dallas **INVITED**

Two-dimensional layered materials, such as graphene and transition metal dichalcogenides (TMDs), have been recently proposed for a number of novel device concepts due to their interesting materials properties. For example, the possibility of low surface defect densities due to an anticipated dearth of surface defects and dangling bonds raises the prospect of improved performance for low power tunnel field effect logic devices that switch on and off very rapidly due to the anticipated steep subthreshold slope characteristic. However, for ALD processes, such surfaces present significant challenges for nucleation and growth. This talk will review our recent work on in-situ characterization of 2D materials for such device applications. This research is supported in part by the STARNet Center for Low Energy Systems Technology, sponsored by the Semiconductor Research Corporation (SRC) and DARPA, the SWAN Center sponsored by the SRC Nanoelectronics Research Initiative and NIST, and by an IBM Faculty Award.

9:00am TF+MS+PS-WeM4 Combining Gas Phase Aerosol Deposition with Atomic Layer Deposition for Fast Thin Film Deposition: A Case Study of Transparent Conducting ZnO, *Elijah Thimsen*, Washington University, St. Louis*, M. Johnson, A. Wagner, A. Mkhoyan, U.R. Kortshagen, E.S. Aydil*, University of Minnesota

Atomic layer deposition (ALD) has emerged as a powerful and scalable technique for a variety of applications where layer-by-layer control over film properties and conformal deposition in tight geometries are needed. One common criticism of ALD is that it is slow and may become uneconomical when thick films and high deposition rates are needed. In fact, deposition rate is often an issue even with physical vapor deposition methods such as sputtering and also chemical vapor deposition. One way to deliver material onto a substrate at high rates is through deposition of nanoparticles. Gas phase aerosol deposition is particularly attractive because rates as high as 100 nm/s are possible even at low temperatures.

However, aerosol deposition often yields porous films unsuitable for optoelectronic applications. In this talk, we describe a new two-step strategy for depositing dense thin films at high rates. Our strategy combines the high rates of aerosol deposition with advantages of ALD. In the first step nanoparticles are synthesized in the gas-phase and deposited onto suitable substrates by aerosol deposition. In the second step, the space between the nanoparticles is infilled by ALD. This is a versatile approach since there are many material options for forming both the nanoparticle network and the ALD coating. In the specific example that will be discussed in this talk, the crystalline nanoparticles are synthesized in a nonthermal plasma containing the precursors that lead to nucleation and growth of the desired material. These nanocrystals are deposited on suitable substrates through supersonic expansion and inertial impaction. Using this approach, we demonstrate fast deposition of nanocrystalline ZnO films, an earth-abundant, nontoxic, low cost material that can be used as a transparent conducting oxide (TCO), from a plasma containing Ar, O_2 and diethylzinc. The space between the particles is filled either by Al_2O_3 or Al-doped ZnO (AZO) to give continuous TCO films. After annealing in H_2 and coating with Al_2O_3, the ZnO nanocrystal network becomes conductive with Hall effect electron mobilities as high as 3.0 cm^2 V^{-1} s^{-1}. Depending on the combination of the nanocrystals, ALD coating, and post processing, we have obtained transparent films with resistivity values as low as 3.8 x10^{-3} Ohm cm. The lowest resistivity films were obtained with undoped ZnO nanoparticles coated with AZO. The resistivity can be improved by doping the nanocrystals, which has proven to be challenging. We will discuss the effects of nanocrystal size, doping of nanocrystals in the gas phase, and film porosity on electrical conductivity.

9:20am TF+MS+PS-WeM5 Detecting Order in the Molecular Layer Deposition of Polymer Films by X-ray Diffraction, *David Bergsman, R.W. Johnson, R. Britto, S.F. Bent*, Stanford University

The deposition of highly ordered, thin, organic films is of great importance to a variety of fields. The development of biological sensors, organic solar cells, and optical devices relies on the ability to grow thin layers of organic material with various thicknesses, compositions, functionalities, and levels of crystallinity. One promising method of creating such films is molecular layer deposition (MLD), which uses an alternating sequence of self-saturating reactions by vapor-phase organic precursors at the substrate to grow films in a layer-by-layer fashion. This technique has been demonstrated with a variety of precursor chemistries and has been shown capable of growing films on high aspect ratio features with low surface roughness and high conformality. But despite the growing use of MLD, many questions still remain as to the orientation of the molecular chains within the deposited films and the packing of these chains. Many different factors may contribute to varying degrees of crystallinity during growth, such as chain-chain steric repulsion, Van der Waals forces, chain growth angle, and inter-chain hydrogen bonding. Here, we demonstrate that some MLD chemistries can form nanoscale organic films that exhibit well-ordered packing. Polyurea MLD films with different thicknesses and backbone chemistries were grown in an MLD reactor and then examined with x-ray diffraction (XRD) using synchrotron radiation at the Stanford Synchrotron Radiation Lightsource (SSRL). Spectroscopic ellipsometry was used to observe film thickness, while x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy monitored for film degradation. XRD results for the polyurea MLD films show peaks at q-values of 1.5/Å, corresponding to a d-spacing around 4.2 Å. Changing the precursor from a more rigid to a more flexible backbone leads to variations in d-spacing and diffraction intensity. Growth on substrates with different surface chemistries and roughness, as well as the effect of heating and re-cooling the films, is also explored. These results suggest that thin organic films with varying levels of packing order can be grown using MLD by tuning the precursor chemistry.

9:40am TF+MS+PS-WeM6 Native Oxide Diffusion and Removal During the Atomic Layer Deposition of Ta_2O_5 on InAs(100) Surfaces, *Alex Henegar, T. Gougousi*, University of Maryland, Baltimore County

The use of high-κ dielectrics on III-V semiconductors in place of Si/SiO$_2$ structures in metal oxide semiconductor devices has been perpetually hindered by poor quality native oxides at the substrate/film interface. A promising solution for the removal of these oxides is the atomic layer deposition (ALD) growth technique which has shown the ability to remove native oxides during deposition without additional processing for certain chemistries.[1–4]

In this work, Ta_2O_5 thin films were deposited on InAs(100) by ALD using pentakis dimethyl amino tantalum (PDMAT) and H_2O to study the effects of film deposition on the native oxides. 3 and 7 nm films were grown at 150-300 °C on InAs substrates covered with native oxides and substrates chemically etched in NH_4OH. Analysis of the film deposited on native oxide covered substrates by x-ray photoelectron spectroscopy (XPS) shows arsenic and indium oxides are readily removed during deposition of 3 nm

Ta_2O_5 at 250 and 300 °C, temperatures very close to the optimal ALD temperature for the specific chemistry. At lower temperatures both oxides persist with indium oxides generally being harder to remove.

Depth profiling by argon-ion sputtering data of 7 nm films shows that indium oxides have diffused into the Ta_2O_5 film. The sharp decrease in oxide signal after the first sputter cycle indicates that the majority of the indium oxide is located near the surface suggesting the migration of indium oxides to the film surface during deposition. Arsenic oxides, however, are detected in smaller amounts and generally speaking remain at the interface. For depositions on etched InAs no arsenic oxides were detected but a small amount of indium oxides remain even at the optimal deposition temperatures. Films grown on etched substrates always contain less indium and arsenic oxides than their equivalents deposited on native oxide surfaces. Mixing of indium oxide in the films may have a significant negative effect on their insulating properties negating any gain from a sharper interface.

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11:00am TF+MS+PS-WeM10 ALD in High Aspect Ratio Structures and Nanoporous Materials, *C. Detavernier, **Jolien Dendooven***, University of Ghent, Belgium **INVITED**

Atomic layer deposition (ALD) is known to be an excellent technique for the deposition of thin films with uniform thickness over micro- and nanoscale 3D structures. The superior conformality of ALD is a direct consequence of the self-saturated surface reaction control and makes the technique increasingly useful in the rapidly growing field of nanotechnology. The successful ALD-based processing of nanostructured materials requires however a careful optimization of the growth parameters. In this work, we present an extensive study on the conformality of ALD in high aspect ratio structures and nanoporous materials.

A first experimental approach was based on the use of macroscopic, trench-like structures in combination with low precursor pressures. In this way, the transport of the precursor molecules in the test structures was governed by molecular flow, as in microscopic trenches under standard ALD conditions. This method allowed us to quantify the conformality of the trimethylaluminum (TMA)/H_2O process as a function of the aspect ratio and the TMA exposure time. Our experimental data indicated that the sticking probability is a determining factor in the conformality of ALD [1]. A better understanding of the effect of this parameter on the conformality was obtained via kinetic modeling and Monte Carlo modeling.

As a second substrate, porous titania thin films with pore sizes in the low mesoporous regime (< 10 nm) were considered in order to get insights on the minimum pore diameter that can be achieved by ALD. Novel in situ characterization techniques were developed to monitor the pore filling by ALD. Synchrotron-based x-ray fluorescence and scattering techniques provided cycle-per-cycle information on the material uptake and densification of the porous film, while ellipsometric porosimetry was used to quantify the pore size reduction. This study nicely demonstrated the ability of ALD to tune the diameter of nanopores down to the molecular level [2].

Finally, we performed ALD of TiO2 into a 3D ordered silica powder with two types of mesopores [3]. By varying the Ti-precursor exposure time, we investigated the introduction of TiO2 into the differently sized mesopores. A TEM study revealed the diffusion limited nature of the TiO2 ALD process, leading to anisotropic penetration profiles in this specific pore structure. We observed a systematic deeper penetration of the deposition front along the main channels compared to the narrower mesopores. These results were corroborated by modeling work.

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11:40am TF+MS+PS-WeM12 Pyrolysis of Alucone MLD Films to Form Electrically Conducting and Nanodomained Al_2O_3/C Composite Films, *J.J. Travis, J.W. DuMont, **Steven George***, University of Colorado, Boulder

Alucone is an aluminum alkoxide polymer grown using molecular layer deposition (MLD) techniques with trimethylaluminum and organic diols or triols as the reactants. Alucone films can be pyrolyzed under inert atmosphere or vacuum to yield electrically conductive Al_2O_3/C composite

films. This pyrolysis provides a pathway to deposit ultrathin, conformal and conducting Al_2O_3/C films on high surface area substrates. Our recent results have shown that the electrical conductance of the Al_2O_3/C films is dependent upon the amount of carbon in the film. The initial alucone films are non-conducting. After pyrolysis to 850°C, alucone films grown using glycerol, with three carbons, or hydroquinone, with six carbons, display high electrical conductivity of ~1-3 S/cm. In contrast, pyrolyzed alucone films grown using ethylene glycol, with only two carbons, remain non-conducting. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the pyrolysis of the alucone films. The C-H, C-O and C-C vibrational features were lost from the alucone films between 300-450°C. The vibrational spectra also showed prominent carboxylate features at 400-450°C. Carboxylate features are consistent with COO^- – Al^{3+} complexes at the interfaces between the Al_2O_3 and carbon regions of the composite. High resolution transmission electron microscopy (HRTEM) images are consistent with a highly interfacial nanodomained Al_2O_3/C composite. These Al_2O_3/C composite films may provide electrical conductivity and oxidation resistance during electrochemical processes on metal and carbon electrodes.

12:00pm **TF+MS+PS-WeM13 Atomic Layer Deposition of Metal Oxides on Ultra-High Aspect Ratio, Vertically Aligned Carbon Nanotube Arrays**, *Kelly Stano*, *M. Carroll, R.P. Padbury, J.S. Jur, P. Bradford*, North Carolina State University

Atomic layer deposition (ALD) is commonly used to coat high aspect ratio structures, including vertically aligned carbon nanotube arrays (VACNTs). Previous studies, however, have demonstrated precursor diffusion depths of only 60 μm for long exposure times, leading to a "canopy effect" where preferential coating takes place at the top of arrays. In this research we report the first example of conformal Al_2O_3 ALD on 1.5 mm tall VACNTs with uniform coating distribution from CNT base to tip. Large-scale CNT arrays with free volume aspect ratios ~15,000 were able to be uniformly coated by manipulating sample orientation and mounting techniques, as confirmed by cross-sectional energy dispersive x-ray spectroscopy. Conformal coating was achieved through modification of CNT surface chemistry via vapor phase techniques including pyrolytic carbon deposition and atmospheric pressure oxygen plasma functionalization. Thermogravimetric analysis revealed that arrays which were functionalized prior to ALD coating were more stable to thermal degradation compared to untreated, ALD coated arrays. Interestingly, CNTs could be easily removed during thermal oxidation to yield arrays of continuous, high surface area, vertically aligned Al_2O_3 nanotubes. Additionally, functionalized and ALD coated arrays exhibited compressive moduli two times greater than pristine arrays coated for the same number of cycles. Al_2O_3 coated arrays exhibited hydrophilic wetting behavior as well as foam-like recovery following compressive strain. These processing techniques have been successfully applied to other ALD precursors to yield CNT arrays uniformly coated with ZnO and TiO_2 as well.

MEMS and NEMS
Room: 301 - Session MN+PS-WeA

Emerging Materials and Fabrication Technologies for MEMS/NEMS
Moderator: Sushma Kotru, The University of Alabama, Meredith Metzler, Cornell University

2:20pm MN+PS-WeA1 Organic Sensors and Actuators Patterned by Inkjet Printing, *Tse Nga (Tina) Ng*, PARC (Palo Alto Research Center), a Xerox Company*, J. Kim, W.S. Kim,* Simon Fraser University, Canada*, K.S. Kwon*, Soonchunhyang University, South Korea **INVITED**
Organic materials have been demonstrated as good candidates for large-area sensors, because they allow wide tolerance of sensor geometry and thickness, which would ease fabrication problems such as strain induced cracking on deformable plastic platforms. Organic electronic materials can be deposited and patterned by low-cost printing tools such as inkjet printers. Notably, the printing process is compatible with many substrates ranging from plastics to fibers, to potentially integrate electronics on any surface. At Palo Alto Research Center, we have developed processes for printed electronics that enable new form factors and applications in flexible sensors and circuits. In conjunction with university collaborators, here we present examples of organic mechanical sensors and actuators fabricated by facile solution processes.

The first example is a capacitive pressure sensor patterned by block copolymers. Different microstructures (hemisphere, cones, nano-needles) are explored for the dielectric film, and the dielectric with nano-needles showed the highest sensitivity, with the relative capacitance change up to 176%/kPa. The capacitor with the nano-needle filler was integrated with an inkjet printed OTFT to provide current output. The device sensitivity is comparable to the sensitivity of human skin and will be useful for tactile sensing applications on a wide range of surfaces.

In a second example, we have fabricated a bimorph actuator from electroactive polymer blends with ionic liquid. The polymer blends allow low-voltage operation, and we found that the actuator displacement increases with larger gradient difference in ionic liquid content. A maximum strain of 0.48% was observed. The electroactive polymers are compatible with extrusion printing and have the potential to be patterned through layer-by-layer printing for incorporation into 3d structures.

3:00pm MN+PS-WeA3 Microfabrication by Etching for Carbon Nanotube Composite Sheets, *Nathan Boyer, J. Rowley, D.D. Allred,* Brigham Young University*, S. Liddiard,* Moxtek, Inc*, R.R. Vanfleet, R.C. Davis*, Brigham Young University
We have prepared extremely smooth carbon nanotube (CNT)/polymer composite sheets and patterned them with holes and trenches using a process of photolithography and plasma etching. The high strength patterned CNT/polymer composite could be used in MEMS applications. A CNT sheet was impregnated with polyimide and the composite was cured in a vacuum hot press at 400°C. A film of amorphous silicon nitride was deposited on the composite sheet and patterned to act as a hard mask during oxygen plasma etching. Structural and mechanical testing of the CNT composite sheets will be presented along with plasma etching results.

3:20pm MN+PS-WeA4 High Aspect Ratio Magnetic MEMS Fabricated using Carbon Nanotube Templated Microfabrication, *Robert Davis, L. Barrett, D. Barton, R.R. Vanfleet, D.D. Allred*, Brigham Young University
We have fabricated nickel microstructures with aspect ratios greater than 20-1, and feature sizes as small as 5 um. The process involves growing a forest of carbon nanotubes in the desired pattern, and coating the tubes with an additional a layer of carbon by CVD. Then the remaining space in the forest, approximately 90%, is filled with nickel by pulsed electroplating. Because the resulting composite has a magnetic response, it is ideal for MEMS magnetic sensors and actuators. To demonstrate this, we constructed a simple MEMS scale sensor with a frame, two flexures and a proof mass. Optical measurement of the proof mass's displacement as a function of applied magnetic field will be shown.

4:20pm MN+PS-WeA7 Sub-100nm Thin Polycrystalline Diamond Nanomechanical Torsional Resonators, *Rui Yang*, Z. Wang, J. Lee, C.A. Zorman, P.X.-L. Feng, Case Western Reserve University
We report experimental demonstration of high-frequency (HF) torsional nanomechanical resonators based on nanoscale polycrystalline diamond thin films. We fabricate devices with tethers as thin as 100nm×50nm in cross section, measure their multi-mode resonances with frequency (f_{res}) into the HF band (up to ~10MHz, while most existing sensitive torsional devices are at kHz or low-MHz), and quality (Q) factors exceeding 2000 at room temperature. We also perform temperature-varying measurements, and observe strikingly different temperature coefficients of frequency (TCf) between the torsional and flexural resonant modes.

Diamond is particularly interesting for micro/nanoelectromechanical systems (MEMS/NEMS), because of its exceptional mechanical properties (Young's modulus greater than 10^{12}Pa), relatively low mass density (3500kg/m^3), very high thermal conductivity (22W/(cm·K)), and excellent wear/corrosion resistivity[1]. Especially, its high sound velocity is attractive for making high frequency mechanical resonators[2]. Resonators based on diamond thin films from microwave plasma chemical vapor deposition have been demonstrated, showing mechanical properties comparable to single crystal. However, *torsional resonators* based on diamond thin films showing resonance in HF band and exceptional force and torque sensitivities have not been explored. While we demonstrated torsional resonators using 1.2µm-thick SiC film[3], *much thinner and smaller devices are required for higher sensitivities.*

Here we fabricate torsional resonators on 50 to 100nm thin polycrystalline diamond films with focused ion beam. We perform Raman spectroscopy to confirm the nanocrystalline diamond nature of the membrane. The mechanical resonances are measured by driving the mechanical motion with a modulated laser (405nm), and detecting the resonant motion with laser interferometry (633nm). These devices show force sensitivity down to the sub-fN/√Hz range, and torque sensitivity on the order of 10^{-22} (N·m)/√Hz, which is similar to the best reported results in other materials[4]. This opens up the possibility for fabricating ultrasensitive devices for force/torque, inertia, and thermal sensing, based on nanocrystalline diamond platform. TCf measurement shows clear and intriguing anti-crossing behavior, which vividly illustrates cross-mode mechanical coupling.

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4:40pm MN+PS-WeA8 Temperature Compensated Graphene Nanomechanical Resonators, *Jaesung Lee*, Case Western Reserve University*, H.-Y. Chiu,* University of Kansas*, P.X.-L. Feng*, Case Western Reserve University
Graphene-based atomically-thin two-dimensional (2D) nanostructures have emerged as new building blocks for novel nanoelectromechanical systems (NEMS) [1], which can enable nanodevices with unprecedented performances such as ultrasensitive detectors and highly tunable oscillators [2] In addition to its excellent mechanical properties, such as ultralow areal density (r_A=0.74fg/µm^2), ultrahigh strain limit (~25%), and large Young's modulus (E_Y~1TP), graphene has superior thermal properties, which can enable large temperature range operations and ultra-stable high temperature performances. In addition, the unique negative thermal expansion coefficient of graphene can be employed to tune the device tension and thus its resonance behavior through controlling the device temperature. To date, most experimental investigations of graphene resonators are at room temperature or below, with high temperature operation remaining largely unexplored.

In this work, we experimentally study graphene resonators from room temperature to ~600K and study their resonance characteristics by measuring the thermomechanical noise. Our graphene resonators show relatively small frequency shifts from 300K to 600K due to natural temperature compensation from the different thermal expansion coefficients of graphene and other structural metals. We further examine temperature profile in graphene resonators, and establish resonator models with wide range temperature operation, elucidating temperature compensation mechanisms in graphene resonators. This study will help improve the understanding and development of both temperature-sensitive and insensitive 2D NEMS resonators, which can lead towards future large temperature range and high temperature application of 2D NEMS.

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5:00pm MN+PS-WeA9 A Porous Material for Improving Cantilever Q in Air and Liquid for Resonant Mechanical Sensing, *Steven Noyce, R.C. Davis, R.R. Vanfleet,* Brigham Young University, *H.G. Craighead*, Cornell University

Nanoporous cantilever resonators have potential performance advantages for cantilever based sensing. For porous cantilevers a high surface area leads to a high adsorbed mass which is independent of the cantilever dimensions. Larger cantilever dimensions can lead to higher quality (Q) factors in air and liquid sensing environments. Here we present work on the fabrication of nanoporous carbon/carbon nanotube composite cantilevers. Our results include characterization work on tuning the composite materials properties and cantilever geometries for high Q in fluid.

5:20pm MN+PS-WeA10 XPS to Investigating Spatial and Temporal Modification of PDMS Platforms for Micro-Fluidic Devices, *Marshal Dhayal*, CSIR- Centre for Cellular and Molecular Biology, India

Spatial and temporal changes in surface chemical composition silicon (Si), carbon (C) and oxygen (O) of polydimethyl siloxane (PDMS) surfaces before and after plasma treatment were estimated from quantitative elemental analysis of X-ray photoelectron spectroscopy (XPS) wide scan spectra. Theoretical ratio of Si/C/O in repeating unit (–[Si-(CH$_3$)$_2$-O]$_n$–) of PDMS were calculated and were compared to experimentally obtained ratio for Si/C/O obtained from untreated and plasma PDMS surfaces used for micro-fluidic devices. The contact angle measurements have shown that (PDMS) surfaces treated by air plasma can recover up to about 50% of its hydrophobic nature in less than 30 min of air exposure. These plasma modified surfaces were functionalized with poly(ethylene glycol) (PEG) silane to obtained PDMS surface as hydrophilic in nature for micro fluidic application. The surface chemistry of PEG-functionalized PDMS substrate has been studied using XPS. These different types of surfaces were used fabricate micro-fluidic devices and effects of surface nature of micro channels on fluid velocity were observed in PEG grafted micro channel in PDMS base micro fluidic devices. The effect of different pH of the fluids on the fluid velocity in PDMS-based micro channel was also studied.

5:40pm MN+PS-WeA11 A Microplasma-based Sputtering System for Direct-Write, Micropatterning of Metal Structures, *Edwin Burwell, A.C. Barnes, P.X.-L. Feng, M. Sankaran, C.A. Zorman*, Case Western Reserve University

Patterning metal as a contact or interconnect is a critical processing step for device fabrication in a wide range of applications ranging from conventional electronics on silicon chips to implantable biosensors on flexible polymeric substrates. Traditionally, physical vapor deposition is combined with photolithography to deposit patterned metal films. Although this subtractive approach produces high pattern fidelity and conductivity, low throughput, materials wastage, and need for vacuum lead to high production costs and limited scalability. The emergence of flexible devices has stimulated the desire for additive approaches such as ink-jet printing for depositing patterned conductive materials. Ink-based printing is carried under ambient conditions and can be integrated with roll-to-roll systems for large-scale manufacturing. However, the inks can be expensive and the variety of materials that are available as printable inks is very small. In addition, the organic capping agents that are used to stabilize the particles are difficult to remove, which can compromise conductivity and mechanical integrity. Removal of the organics requires high annealing temperatures that limit the usage of certain polymers and other temperature-sensitive substrates. Adhesion of the printed structures to the substrates can also be a significant issue, especially in flexible applications.

In this paper, we describe a microplasma-based process to deposit patterned structures with micro- to nanoscale dimensions on rigid or flexible conducting and insulating substrates. This direct-write, additive process uses plasma-based sputtering to generate a physical vapor comprised of the material of interest. The plasma is generated within a small capillary tube that is capped with a micron-sized orifice. The sputtering target consisting of a micron-sized wire is positioned inside the capillary. Forced Ar flow aids in the ejection of the resulting physical vapor through the orifice, which is positioned in close proximity to the substrate. The process is performed at atmospheric pressure, thereby addressing the most significant limitation associated with conventional magnetron sputtering and thermal evaporation, and is low temperature, allowing deposition on temperature-sensitive substrates such as polymers and paper. To date, we have successfully deposited patterned Au structures that are submicron in thickness and 150

microns in width on glass substrates. Our presentation will detail the apparatus, the principal of operation, and the most current results in creating and characterizing micropatterned metal structures on insulating substrates.

Plasma Science and Technology
Room: 305 - Session PS+2D-WeA

Plasma Processing for 2D Materials, Coating, and Surface Modification
Moderator: Colin Wolden, Colorado School of Mines

2:20pm PS+2D-WeA1 Hydrogen Plasmas Processing of Graphene, *Emilie Despiau-Pujo, A.O. Davydova, G. Cunge*, LTM, Univ. Grenoble Alpes/CNRS/CEA-Leti Minatec, France, *L. Magaud*, Institut Neel, Univ. Grenoble Alpes/CNRS, France, *D.B. Graves*, University of California at Berkeley **INVITED**

The successful development of graphene-based technologies relies on our capability to grow and integrate this new material into sophisticated devices. Since the presence of multilayers or defects/contaminants on the graphene surface can significantly degrade its intrinsic properties, the development of new techniques to clean graphene surfaces from polymer residues, etch graphene films layer-by-layer or pattern graphene nanoribbons (GNRs) with minimal edge disorder, are major challenges. ICP H$_2$ plasmas seem promising to specifically treat graphene films but little is known about the fundamental mechanisms of plasma-graphene interaction. We therefore develop Molecular Dynamics (MD) simulations, coupled with experiments, to assist the development of plasma processes to clean, dope and pattern graphene layers in a controlled way. We more specifically investigate the interactions between hydrogen plasmas and various types of graphene surfaces (monolayers, multilayers, nanoribbons). Except for impacts at GNRs edges or defects location, H species are shown to experience a repulsive force which prevents any species with less than ~0.6eV to adsorb on the graphene surface. H$^+$ bombardment in the [1-10] eV range does not damage the graphene basal plane while irreversible damages are expected for $E_i >12$ eV (penetration of atomic H through the layers or C-C bond breaking) [1]. As a first step to model graphene cleaning, we investigate the mechanisms of CH$_3$ groups (a crude approximation for resist residues) removal from graphene by atomic hydrogen. Depending on the incident energy range and the surface temperature, MD shows the possibility for chemical etching of the methyl radical without damaging the graphene basal plane [2]. Recent experiments and XPS/AFM/Raman measurements confirm that H$_2$ plasmas are promising to clean PMMA residues from graphene with almost no damage after annealing. Simulations of GNRs trimming show that lateral etching is maximum for surface temperatures ~600 K and occurs via a specific mechanism limiting the edge roughness, as also observed experimentally. Finally, energetic H$^+$ or H$_2^+$ bombardment of stacked multilayer graphene (s-MLG) is investigated and the possibility to store hydrogen (trapped as H$_2$ molecules) between adjacent layers or etch a full single graphene sheet is discussed. [1] Despiau-Pujo, Davydova, Cunge et al, J.Appl.Phys.113, 114302 (2013) [2] Delfour, Davydova, Despiau-Pujo et al, submitted to Phys.Rev.B (2014)

3:00pm PS+2D-WeA3 Plasma Synthesis of WS$_2$ Films, *Rachel Morrish, C.D. Sentman, T. Haak, C.A. Wolden*, Colorado School of Mines

Two-dimensional metal dichalcogenides (WS$_2$, MoS$_2$) have attracted great interest due to their extraordinary optical properties, catalytic performance, and electronic structure. Synthesis of WS$_2$ has been accomplished by a variety of methods, but the high temperature (> 800 ºC) and/or harsh S atmosphere required by many of these procedures precludes deposition onto conductive layers and low-temperature glass substrates needed for many applications. Previously we demonstrated the advantages of plasma processing for low temperature synthesis of a related metal dichalcogenide, pyrite (FeS$_2$). It was shown that stoichiometric FeS$_2$ films could be fabricated either by plasma-assisted sulfurization of hematite [1] or by direct deposition using pulsed plasma-enhanced chemical vapor deposition (PECVD) with mixtures of H$_2$S and Fe(CO)$_5$. [2] In this talk we describe how these two approaches may be readily extended to the synthesis of WS$_2$ using WO$_3$ and W(CO)$_6$, respectively.

Thin tungsten disulfide (WS$_2$) films were prepared on FTO coated glass substrates by H$_2$S plasma sulfurization of sputtered WO$_3$. The reactive environment provided by the plasma enabled the complete transformation of oxide films to stoichiometric WS$_2$ within one hour at 500 °C. An apparent activation energy of 63.6 ± 1.9 kJ/mol was calculated for the plasma conversion process, which is less than half the barrier reported for the reaction of WO$_3$ with H$_2$S. The conversion followed Deal-Grove behavior, with the growing WS$_2$ overlayer hindering diffusion to/from the

reactive interface. Calibrated light absorption and relative intensity of the second order Raman 2LA(M) peak were identified as two additional methods to progressively monitor the thickness of the WS_2. The semiconducting WS_2 layers exhibited *n*-type behavior with an indirect band gap at 1.4 eV and an absorption coefficient of $\sim 5 \times 10^4$ cm^{-1}. Self-limiting growth of WS_2 thin films was accomplished by pulsed PECVD with continuous delivery of tungsten hexacarbonyl diluted in a mixture of H_2S and argon. The growth rate per cycle was controlled between 0.1 – 1 Å/pulse by adjusting the precursor flowrate. It was found that the morphology and orientation of the films was a complex function of film thickness, substrate temperature, and plasma parameters. Preliminary electrochemical measurements showed that these WS_2 films reduced the overpotential required for the hydrogen evolution reaction by several hundred mV relative to FTO while displaying good stability.

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3:20pm PS+2D-WeA4 Decoration of Graphene with Gold Alloy Nanoparticles Synthesized in Solution Plasma, *Maria Antoaneta Bratescu*, Aichi Science and Technology Foundation, Nagoya University, Japan, *T. Ueno, N. Saito*, Nagoya University, Japan
In order to be used in electronics and optics, graphene must be in contact with other materials, which can change its electrical and optical properties. The substrate, charge impurities, doping with chemical functional groups, and metal contacts can shift the position of the Fermi level of graphene. Furthermore, graphene with plasmonic nanoparticles (NPs) can offer a new perspective for light conversion systems, by optimization of visible light absorption via the SPR of the NPs, followed by electron exchange between graphene and NPs and electron transport through graphene.

In this work we present a facile, one-step, and surfactant-free method for the synthesis and loading of stable gold and gold-alloy NP on large-area graphene without NP deterioration using an electrical discharge in a liquid solution, termed solution plasma (SP). We investigated the charge transfer process between graphene and gold-alloy NPs by Raman spectroscopy and electron energy loss spectroscopy (EELS) in high resolution transmission electron microscopy (HRTEM).

The excess charge on graphene caused by transferred electrons or holes from the NPs to graphene was calculated from the change of the Fermi level relative to the initial position and the shift of the G band. In the case of graphene with gold NPs a decrease of the surface charge concentration with -3.5×10^{12} cm^{-2}, and a movement of Fermi level with -0.06 eV.

In the case of the AuIn and AuGa NPs the transfer of electrons from graphene to the gold-alloy NPs produces an increase of the surface charge with 1.3×10^{12} cm^{-2} and 1.9×10^{12} cm^{-2}, which correspond to a raising of Fermi level with 0.02 eV and 0.03 eV, respectively.

The EELS results were consistent with Raman spectroscopy results, i.e. the electrons and holes are transferred from the gold and gold-alloy NPs to graphene, respectively.

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4:20pm PS+2D-WeA7 Generation and Stabilization Mechanisms of Free Radicals in Plasma Polymers, *S. Ershov, F. Khelifa, P. Dubois, Rony Snyders*, University of Mons, Belgium
Cladded aluminum alloys are widely used in many applications being protected by a conversion coating based offering some self-healing properties nowadays based on the use of toxic chromate compounds. For both environmental and work safety reasons it is necessary to identify an alternative to this chromate-based conversion coating (CBCC).

In this context, in the framework of a collaborative project, we are working on the replacement of the CBCC by a multilayer combining, among others, plasma polymer films (PPF) and conventional polymers. The key features of this multilayer is grafting of a conventional polymer on the alloy surface by using the free radicals present in the as-deposited PPF as initiating sites for a radical-based polymerization reaction. It is therefore necessary to get a complete understanding on the generation and stabilization of the PPF radicals in order to control the grafting procedure.

The aim of this work is to contribute towards the understanding of the free radicals generation mechanism in the PPF and on their stabilization by comparing the plasma polymerization of different precursors namely isopropanol, benzene and cyclohexane. *In situ* FTIR spectroscopy and a combination of XPS and chemical derivatization measurements are used to quantitatively evaluate the plasma and thin films chemistry, respectively.

Grafting experiments with 2-ethylhexyl acrylate (EHA) allows to cross-check the relevance of the XPS results.

Our results reveal that, for isopropanol PPF, the surface density of free radicals is about $\sim 1.6 \cdot 10^{14}$ spin/cm^2 and depends strongly on the injected power in the plasma. On the other hand, a significant effect of the presence of resonant structure in the plasma polymer on the radical stability is highlighted.

4:40pm PS+2D-WeA8 Simulation of Direct Current Microplasma Discharge in Carbon Dioxide at High and Intermediate Pressures, *N. Hasan, P.R. Fernandez, Bakhtier Farouk*, Drexel University
Direct current (DC) micro-plasma discharges in intermediate to high pressure (10~200 kPa) carbon dioxide are investigated for potential applications in carbon dioxide decomposition and thin film deposition. Numerical simulations are performed using a hybrid CFD model. The model contains detailed reaction mechanisms for the gas-phase discharge and the surface reactions to predict the species densities in the discharge and the deposition characteristics and its growth rate. Sixteen species and a seventy-six step reaction mechanism are considered for the gas-phase carbon dioxide discharge. A simplified surface chemistry consisting eleven reaction steps are considered in the model. The simulations are carried out for a DC pin-to-plate electrode configuration with an inter-electrode gap of 500 μm. An external circuit is also considered along with the discharge model and surface reactions. Basic plasma properties such as electron and species density, electric field, electron temperature and gas temperature are studied. Special attention is devoted to study the influence of operating pressure and discharge current on the plasma characteristics and the deposition characteristics and its rate. The CO2+ and O- concentrations are found to be the dominant ions in the plasma. The simulations indicated significant gas heating in the entire regime of operation. Ion Joule heating was found to be dominant in the sheath whereas Franck–Condon heating and heavy particle reaction induced heating was dominant in the volume. The results presented here can be utilized for the development of computational models for plasma discharge in supercritical conditions which can be used to investigate processes such as carbon nanotube synthesis, biological reaction catalysis and carbon dioxide decomposition.

5:00pm PS+2D-WeA9 The Impact of Ambient Gas Chemistry on Lipopolysaccharide Deactivation and Polymer Modification by Plasma-Generated Radicals at Atmospheric Pressure, *Elliot Bartis, A.J. Knoll, P. Luan, C. Hart,* University of Maryland, College Park, *D.B. Graves,* University of California, Berkeley, *I.V. Adamovich, W. Lempert,* The Ohio State University, *J. Seog, G.S. Oehrlein,* University of Maryland, College Park
In this study, lipopolysaccharide (LPS) -coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. The goal of the present work is to understand the role of plasma-environment interactions in biodeactivation and surface modifications by regulating both the proximity of the plasma to the environment and the environmental gas chemistry. The APPJ is mounted inside a vacuum chamber that can be evacuated and refilled with any gas chemistry. By changing the APPJ geometry, the plasma plume can be either exposed or protected from the ambient. By adding small N_2/O_2 admixtures to Ar, we find that the O_2 admixture in the APPJ is a major determining factor for both deactivation and surface modification as measured by an enzyme-linked immunosorbent assay and x-ray photoelectron spectroscopy, respectively. N_2 admixture without O_2 causes minimal deactivation, while N_2/O_2 admixtures deactivate more with increasing O_2 content. For identical O_2 feed gas flows, less deactivation occurs when N_2 is also added, which demonstrates that nitrogen-based species quench reactive oxygen species (ROS) responsible for biodeactivation. After plasma treatments, a new chemical species was detected on LPS surfaces that was stoichiometrically verified as NO_3. To determine if this species forms due to nitrogen and oxygen found naturally in LPS, we treated model polymer films of polystyrene, polypropylene, and poly(methyl methacrylate), as these materials contain solely carbon or only carbon and oxygen. We find that the formation of NO_3 is generic to all surfaces even with no N_2 in the feed gas. Thus, the reactive interaction of oxygen-based species with ambient N_2 takes place, indicating that plasma-environment interactions create this moiety and providing insight into the mechanisms by which the APPJ modifies surfaces. For polystyrene films, oxygen uptake is dramatic with O/C ratios as high as 0.47 at the near surface. The oxygen uptake results in a variety of moieties including C-O, O-C-O, C-O-NO_2, O-C=O, and O-(C=O)-O. APPJ treatments are also compared with a corona discharge to examine the role of long lived species such as ozone and NO_x. Results from gas-phase characterization will also be discussed. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

5:20pm PS+2D-WeA10 Modification of LDPE Induced by an Ar/H₂O Plasma: Comparison between a Post-Discharge Treatment and a DBD Treatment, *Stephanie Collette*, Université Libre de Bruxelles, Belgium, *V. Cristaudo*, Université catholique de Louvain, Belgium, *T.R. Dufour*, Université Libre de Bruxelles, Belgium, *P. Viville*, Université de Mons, Belgium, *A. Delcorte*, Université catholique de Louvain, Belgium, *F.A.B. Reniers*, Université Libre de Bruxelles, Belgium

The study of the water reactivity in plasma was achieved by injecting water vapor in the post-discharge of an RF plasma torch and in a dielectric barrier discharge (DBD), both supplied in argon as carrier gas.

The RF plasma torch operates at atmospheric pressure. Optical emission spectroscopy (OES) and mass spectrometry evidenced the production and the consumption rates of Ar, O, OH, O_2^+ and N_2 species. These species could be quantified as a function of the water vapor flow rate, the treatment time and the gap (distance separating the post-discharge from a solid surface) to have a better understanding of the reactivity. Some chemical reactions occurring within the post-discharge could be evidenced and their importance was determined according to their kinetic constants. The reactivity of H_2O in the post-discharge was also carried out using an indirect method: the exposure of low density polyethylene (LDPE) samples to the plasma torch, in order to correlate the amount of oxygenated radicals resulting from water vapor dissociation reactions with the amount of oxygenated functions (C-O, C=O, COO) grafted on the surface. The modified LDPE surfaces were characterized by X-ray photoelectron spectroscopy (XPS), with a special emphasis on the deconvolution of the spectral envelope of the C1s peak. For longer treatment times, we showed that the decrease in the oxygen concentration observed by XPS could result from a competition between the LDPE surface etching and its functionalization. Besides, depth profiles achieved with XPS evidenced the diffusion of O in the subsurface, thus proving the efficiency of the plasma treatment. Those results were correlated with WCA measurements indicating a decrease of the angle from 100° to 35° and with AFM showing an increase of the RMS roughness value from 30 nm to 90 nm. ToF-SIMS analyzes were also achieved on LDPE surfaces. To compare the impact of the plasma treatment to the influence of water contained in the atmosphere, D_2O was injected in the plasma torch. The use of D_2O permits to selectively probe the presence of fragments from the injected water grafted on the LDPE surface.

Those results were compared to those obtained with a second plasma source, namely a DBD operating at atmospheric pressure. In this case, LDPE samples were placed directly between the two dielectric barriers. Similar species as those described in the post-discharge have been evidenced by OES and MS with however slightly different reactive mechanisms, thus explaining why the treated LDPE surfaces present a different hydrophilic state.

This work was supported by PSI-IAP 7(plasma surface interactions (Belgian Federal Government BELSPO agency)).

5:40pm PS+2D-WeA11 Atmospheric Plasma Polymerization of Fluorinated Precursor : Comparison of Various Liquid Precursors and Plasma Types (AC and Pulsed DC), *J. Hubert, Nicolas Vandencasteele*, Université Libre de Bruxelles, Belgium, *C. Poleunis*, Université catholique de Louvain, Belgium, *J. Mertens*, Université Libre de Bruxelles, Belgium, *A. Delcorte, P. Bertrand*, Université catholique de Louvain, Belgium, *F.A.B. Reniers*, Université Libre de Bruxelles, Belgium

The deposition of PTFE like films by argon atmospheric plasma using various precursors, liquid at room temperature, is presented. Those compounds are: Perfluorohexane (C_6F_{14}), a fully saturated monomer, perfluoro(2-methylpent-2-ene) (C_6F_{12}) containing one unsaturated bond and Perfluorotributylamine ($C_{12}F_{27}N$), containing a central nitrogen atom to which 3 fully saturated perfluorobutyl chains are attached. The influence of the monomer structure as well as the electrical parameter of the plasma (AC or pulsed DC) on the films chemistry and deposition rate is studied.

PTFE like films are of interest because of their low surface energy which gives them interesting properties such as easiness of cleaning etc.

The surface composition of the films is studied by X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface energy of the films is studied by Water Contact Angle (WCA). The films thickness is determined by profilometry, and the composition of the plasma phase is analyzed by atmospheric Mass Spectrometry (atm-MS) and Optical Emission Spectroscopy (OES).

Results

Very similar atomic composition and surface energies are obtained for the tested range of experimental parameters. Difference in composition, depending on the precursor used, can however be detected in the high resolution C1s peak (XPS). The signature of the precursor can also be detected in the atm-MS results of the plasma phase. OES measurements on the other hand do not allow to easily differentiate the various precursors.

The main species detected other than Ar are F and CF_2. The combination of the gas phase analysis and the films composition suggest a small fragmentation of the monomer in the plasma. Indeed as the initial structure of the precursor can still be detected in the deposited films we can conclude that the chemical structure of the polymerizing species must be close to the one of the initial molecule.

Differences in deposition speed depending on the precursor type and/or the plasma type (AC or DC) are evidenced by profilometry measurements. As expected the precursor containing the unsaturated bond has a higher deposition rate. Thicker films exhibit slightly higher contact angle values (~140°) than thinner ones (~130°). This cannot be attributed to the chemical composition of the films as they are very similar but can be explained by the increased roughness of the thicker samples.

The overall composition of the films can only be slightly modified by changing the precursor structure or the plasma parameters. The deposition speed is the main parameters linked to both the precursors structure and the plasma parameters.

6:00pm PS+2D-WeA12 Surface Modification of Nafion Membranes Exposed to an atmospheric He-O₂ and He-H₂ Post-Discharge, *Thierry Dufour*, *D. Merche, H. Julie, R.F. François*, Université Libre de Bruxelles, Belgium

Nafion is commonly used as a proton-conducting polymer membrane to separate the anode and cathode compartment of proton exchange membrane fuel cells (PEMFC) and water electrolyzers. The use of plasma based technology has contributed to lower catalyst loadings, thus decreasing the production costs. In this framework, our researches have been focused on a simple and robust technique to modify Nafion surface properties, using the post-discharge of an atmospheric RF plasma torch supplied in helium as carrier gas and H_2 or O_2 as reactive gas. The modifications achieved on Nafion samples have been compared with those of common polymers such as polyethylene, PVF and PTFE. Contrarily to these polymers, the Nafion presents more complex etching mechanisms, that may be correlated with the complexity of its molecular formula: (i) its hydrophobic region is a continuous semi-crystalline region which is Teflon®-like, being made up of main chain TFE segments, while (ii) its hydrophilic region (sulfonate group) allows water and proton/ion transport but can also swell and change in size and/or shape with water uptake (eventually forming a continuous network). We have already demonstrated that the chemical nature of the fragment species (ejected from the Nafion film) depends on the exposure time because the fluorinated backbone is not etched as efficiently as the perfluorovinyl ether groups terminated with sulfonate groups.

The morphological and chemical structural changes of the Nafion films during exposure to the post-discharge have been characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as WCA (Water Contact Angle) measurements. Moreover, a characterization of the proton conductivity and of the methanol permeability will also be introduced.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency.

Plasma Science and Technology
Room: 308 - Session PS-WeA

Plasma Diagnostics, Sensors, and Control
Moderator: Jean-Paul Booth, LPP-CNRS, Ecole Polytechnique, France

2:20pm PS-WeA1 Diagnostics of Cl₂/O₂ Inductively-Coupled Plasmas by Ultra-High Sensitivity Broad-Band Absorption Spectroscopy, *Mickaël Foucher*, LPP-CNRS, Ecole Polytechnique, France, *E. Carbone*, LTM - MINATEC - CEA/LETI, France, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France

Inductively-coupled plasmas (ICP) containing O_2 and Cl_2 (and often HBr) are widely used for etching, for example of silicon transistor gate. Simulations, including global and two-dimensional fluid models have been developed over the years, but validation against experimental measurements of absolute densities remains sparse.

Absorption spectroscopy is a powerful diagnostic for reactive plasmas, providing absolute density measurements of numerous atoms, molecules and free radicals in ground and various excited states. The sensitivity is determined in practice by the characteristics of the light source used: spectral range, stability and intensity. Previously Xe arc lamps have been used but they suffer from spatiotemporal fluctuations, limiting the sensitivity to about 10^{-3} in absorption. More recently UV light-emitting

diodes have been used, giving greatly increased stability, but these have very limited spectral ranges (a few 10's of nm), necessitating the use of specific diodes for each species detected.

We have constructed a new absorption bench that overcomes these difficulties. The light from a broad-band (200-1000) nm laser-induced plasma source (Energetiq-LDLS EQ-99) is collimated and steered with reflective (achromatic) optics. After passing through the reactor the beam is analyzed with an aberration-corrected spectrograph (Acton SCT-320) equipped with a 1024 element photodiode array detector. Three gratings allow spectral ranges of 32, 63 or 250 nm to be analyzed at one time. This setup gives spectra in minutes with random noise and baseline stability better than 10^{-4}, allowing detection of species which only show weak absorption bands over wide spectral ranges.

The gases (O_2, Cl_2 and mixtures) are flowed through a cylindrical aluminum chamber (55 cm diameter, 10 cm height). The plasma is excited at 13.56 MHz by a 4-turn planar coil through a dielectric window. We observed molecular absorption bands from ground state Cl_2, vibrationally excited O_2 and of various O_xCl_y reaction products, allowing the densities, vibrational and rotation temperatures to be determined. As far as we know this is the first time oxychlorides densities have been measured in plasmas. This data is complemented by measurements of absolute atom densities (Cl and O) by TALIF and hairpin probe measurements of electron density. The interpretation of this data set will be discussed.

2:40pm PS-WeA2 Diagnostics in Pulsed Hydrogen Plasmas, *Jerome Dubois*, *G. Cunge*, LTM - CEA/LETI, France, *N. Posseme*, CEA-LETI, France, *M. Darnon*, LTM - CEA/LETI, France, *L. Vallier*, CNRS-LTM, France, *O. Joubert*, LTM - CEA/LETI, France

Hydrogen plasmas have been used for decades in the microelectronic industry with applications in the fields of deposition (PECVD, Plasma Enhanced Chemical Vapor Deposition) [1], etching [2] and surface treatment (reduction of the photoresist roughness in the lithography step [3]). However hydrogen is a very peculiar element due to his low mass and his electronegative character, and the mechanisms at stake in low pressure hydrogen plasma aren't well understood yet. A complete fundamental study with reliable diagnostics would be highly valuable for many applications [4]. Moreover, hydrogen plasmas present a great potential interest for the treatment of new materials such as graphene [5] or carbon nanotubes [6]. To modify the surface of such ultrathin layers without damaging the material, very low ion energy bombardment is required (conditions such as those obtained in pulsed ICP reactor [7]). By contrast, for other applications such as etching of several nanometer thick layers, the ion energy must be very high to get a significant etch rate. To assist the development of innovative processes in H_2 plasmas, we have thus analyzed systematically CW and pulsed H_2 plasmas both with and without RF bias power. In particular, we carry out time-resolved ion flux, and time-averaged ion energy measurements in different pulsing configurations. A large variety of ion energies and shapes of IVDF are reported depending on pulsing parameters. The IVDF are typically very broad (due to the low ion transit time of low mass ion through the sheath) and either bi or tri-modal (H^+, H_2^+ and H_3^+ contributions). The time variations of the ion flux in pulsed plasmas also presents peculiar features that will be discussed.

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3:00pm PS-WeA3 The Role of Diagnostics in Plasma Etch Reactors in Enabling the Information Age, *Alex Paterson*, *J. Holland, S. Sriraman, E. Hudson, H. Singh, V. Vahedi*, Lam Research Corp **INVITED**
Over the last decade, semiconductor industry growth has been driven chiefly by the demand for consumer electronics: the move to mobile smart devices such as phones and tablet PC's. It is now common place for hand-held mobile devices to have 32 Gb of memory and processor speeds of over

1 GHz, a truly remarkable feat that would have been unthinkable 10 years ago. This capability has been enabled by the continuation of IC scaling to smaller and smaller features sizes with the present technology being mass produced by 28 nm node technology and smaller nodes down to 10 nm currently being developed by IC manufacturers. The limitations of lithography to keep up with the decrease in dimensions required for these smaller nodes has resulted in new challenges for plasma etch to enable patterning at these small feature sizes. Device performance requirements also drive critical dimension (CD) non-uniformity to less than one nanometer across the entire 300 mm wafer for sub-20 nm features and yield requirements extend this pattering region to within 1.5 mm of the wafer edge. Wafer fabrication production also relies on plasma etch solutions to be stable at these levels across long periods of time and capable of flexibility in multiple applications. The realization of all of these goals has been greatly facilitated by a much better understanding of the basic chemical, physical, and electromagnetic processes that occur during the plasma etch of semiconductor devices.

In this paper we will discuss the crucial role diagnostics play in achieving this understanding and in the development of state of the art plasma etch chamber technology that allow the continuation of Moore's Law. Diagnostics are essential not only to understand etch mechanisms and chamber characteristics but to also accelerate hardware development in order to meet customer time critical needs. We will review the different types of diagnostics commonly used in plasma etch chamber development with reference to findings from literature and augment this with diagnostic work undertaken at Lam Research. Finally, we will discuss the suitability of diagnostics in main stream production and give some thoughts on future diagnostics that may be required for production enhancement and also angstrom level etching.

4:20pm PS-WeA7 Ion Angular Distributions Measured with a Planar Retarding Field Analyzer, *Shailesh Sharma*, Impedans Ltd., Ireland
In microelectronics fabrication the angular distribution of the bombarding ions can impact the process outcome. The ion energy distribution as a function of ion angle at specific locations on the substrate or wafer surface need to be controlled in certain anisotropic etching and conformal deposition plasma processes. We report a novel method for the measurement of ion energy distributions as a function of ion angle, at the substrate location, using a planar retarding field analyser.

Planar retarding field analyzers are commonly used to measure ion energy distributions but provide no information about the angular distribution of ions bombarding the substrate surface. Here, we report on a novel planar retarding field analyser design capable of resolving the angular distribution of the energetic ions. The design has three active grids, a collector plate and an aperture with variable aspect ratio (height / diameter) to control the angular spread of the ions allowed through the device for detection. First, the potential of the ion energy discriminating grid is modulated to select ions with a specified energy resolution for analysis. Then, the aspect ratio of the aperture is varied from large acceptance angle to narrow acceptance angle with specified angle resolution - predetermined from the aperture geometry. The ion current is recorded for each acceptance angle to give an integral form of the ion angular distribution at a given ion energy where the angular distribution can be recovered by taking a first derivative. The procedure is then repeated for each ion energy. Once the angular distribution is determined as a function of ion energy, the energy distribution as a function of ion angle is easily calculated.

The analytical theory used to define ion current as a function of incident ion angle, ion energy and aperture aspect ratio is presented. The method used to vary the aspect ratio of the additional aperture is also discussed. This novel method allows ion angular distributions to be determined using a compact planar retarding field analyser.

With the modified retarding field analyzer design and advanced analytical technique, ion angular distributions with angle resolution as low as 3° have been measured and resolution up to 1° can be achieved. This technique adds important functionality to the retarding field analyser technology - which has become one of the most important technologies in the field of plasma diagnostics in recent years.

4:40pm PS-WeA8 Quantitative Analysis of Neutral Species Generated in Styrene Low Pressure RF Plasma, as a Function of Plasma Power, *X. Gillon, J.-J. Jean-Jacques, Laurent Houssiau*, University of Namur, Belgium
Plasma polymerization processes enable unique polymer coatings unattainable with conventional wet chemistry. Among them, plasma polystyrene (pPS) deposition has been intensively studied, but very few studies report on plasma diagnostics of styrene discharges, which is however a necessary step to understand the fundamental mechanisms of plasma polymerization. In this work, pPS was produced from pure styrene vapor injected in a vacuum chamber at 50 mTorr (6.7 Pa) and 28 sccm. An

inductively coupled plasma was ignited by a planar coil delivering a continuous wave RF power ranging from 30 W to 210 W. Plasma diagnostics was achieved by means of a mass spectrometer (MS) located in the post-discharge region, enabling only the detection of neutral species. A problem associated with electron impact MS is the cracking of organic molecules, which hampers species identification and quantification in the plasma phase. However, by reducing the electron energy as low as 12 eV, much below the standard 70 eV energy, we were able to suppress most of the molecular cracking, so that species measured by MS could be unambiguously assigned to neutral species existing in the plasma. The assignment was further confirmed by measuring the appearance potentials of all ions in the MS. This procedure revealed the existence of 55 neutral species in the styrene plasma, which is five times more than what has been reported so far. Their relative intensities in the MS spectrum help understanding the formation pathways of these species, either by direct fragmentation of the styrene molecule, or by recombination of small molecules. The most abundant species generated in the styrene plasma were H_2, methane, acetylene, ethylene, benzene, toluene and naphthalene. In order to quantify the partial pressure of those species in the plasma, we determined their sensitivity factors by injecting them pure in the plasma reactor and measuring the molecular ion peak intensity at 50 mTorr pressure. The MS intensities measured in the styrene plasma were subsequently converted into partial pressures. The sum of partial pressures from the main species present in the plasma, including styrene, was found to match remarkably well with the measured pressure in the reactor, confirming the quantitativeness of the procedure. The main features observed in the plasma chemistry when the power was raised are: a decrease of styrene pressure (monomer consumption) along with a strong production of acetylene and hydrogen. A very sharp drop of the plasma pressure was measured around 185 W, corresponding to the disappearance of the monomer and a sudden increase of the deposition rate.

5:00pm **PS-WeA9 Comparison of Commercial Plasma Probe Systems**, *Valery Godyak*, RF Plasma Consulting, *B.M. Alexandrovich*, Plasma Sensors

Electrostatic (Langmuir) probes are powerful instruments for diagnostics of non-equilibrium plasmas in experimental and industrial plasma reactors. There are three levels of the probe diagnostics comprising different equipment complexity and having different accuracy of obtained the plasma parameters. These three approaches are based on inferring the plasma parameters from: *i* – the ion part of the probe characteristic, *ii* – the electron part of the probe characteristic (classical Langmuir probe method), and *iii* - by differentiation of the probe characteristic to obtain an Electron Energy Distribution Function, EEDF. Then, the electron temperature T_e and plasma density N, as well as, the rates of collisional processes and transport coefficients are found as corresponding integrals of the measured EEDF. Methods *i* and *ii* assume Maxwellian EEDF which is not valid for most cases of non-equilibrium plasmas. This and many others questionable assumptions in methods *i* and *ii* make actual EEDF measurements the only reliable contemporary probe diagnostics. Langmuir probes in plasma processing reactors are often subjected to the probe surface contamination and high level of rf and low frequency noise. Reliable EEDF measurements require the probe system capable of efficient mitigation of these environmental distortions. The presentation main subject is comparison of EEDF measurement results obtained with different commercial probe systems. It is shown that the measurement accuracy of the plasma parameters in many commercial probe systems is compromised by heavily distorted EEDF in low and high energy region. Low energy distortions make impossible to detect low energy electrons (comprising the majority of electron population), thus leading to underestimation of the plasma density, while high energy distortions make impossible detection of fast electrons producing excitation and ionization. Therefore, some commercial probe systems yielding distorted EEDFs are unable to reveal any additional valid information to that obtained with classical Langmuir procedure.

5:20pm **PS-WeA10 Systematic Diagnostic Approach for Fabricating High Quality SiNx:H Film using UHF Assisted Capacitively Coupled Plasma Source**, *J.G. Han, B.B. Sahu, **Kyung S. Shin**, Sungkyunkwan University, Republic of Korea, *K. Ishikawa, M. Hori*, Nagoya University, Japan

Silicon nitride thin films have shown many useful applications in microelectronic and optoelectronic industries. Fabrication, of these films at low temperature, is done typically by PECVD using a mixture of silane (SiH_4) and ammonia (NH_3). Recent trend shows that the most practical deposition of low-hydrogen-content-silicon-nitride-films (SiNx:H) is to use N_2 instead of NH_3 as the main nitrogen source. However, N_2 has an inherently much higher bonding energy than NH_3, which makes N_2 more difficult to dissociate into free nitrogen active species, thus nitrogen deposition rate is significantly reduced. But if low hydrogen nitride films can be obtained, which may give better device performance, the deposition

rate may not be an important factor and PECVD of silicon nitride by little addition of SiH_4 and NH_3 to the N_2 is still an attractive process. Moreover, the important deposition parameters for any PECVD process are RF power, working pressure, substrate temperature, the gas flow ratio of the reactant gases and the electrode spacing (for CCD or parallel plate system). All these parameters have significant role on the deposition and etch rates along with other physical and optical properties of film depending on device applications.

Although PECVD processes have shown as an emerging method for achieving good quality SiNx:H films for the industry, still there are lack of understanding in correlation between the properties of the plasmas and the characteristics of the synthesized films. In the present work, a deposition parameter matrix is constructed for N_2-SiH_4-NH_3 PECVD process and the effect of variation of above parameters on deposition is studies. The present study investigates PECVD process with different plasma processing conditions by utilization of different plasma sources, e.g., RF, which is capacitively coupled plasma (CCP) source at 13.56 MHz and UHF, a 320 MHz very high frequency (VHF) RF source. The goal of the UHF source is to assist and enhance the dissociation of nitrogen radicals along with the RF. One of the major goals of this work is also to investigate dissociation of the nitrogen radicals, which controls the SiNx:H film deposition process. To understand the fundamental plasma surface interactions in this process, basic plasma diagnostics such as Langmuir probe (LP), optical emission spectroscopy (OES), and vacuum ultraviolet absorption spectroscopy (VUVAS), etc., are used. Thus, the investigations, of high quality SiNx:H film synthesis described in this paper, focus predominantly on the plasma diagnostics and film synthesis. This also reports about high quality film having transmittance about 90 %.

5:40pm **PS-WeA11 Electron Beam Generated Plasmas in Fluorine Chemistries**, *David Boris*, *R.F. Fernsler, G.M. Petrov, Tz.B. Petrova, S.G. Walton*, Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma densities and very low electron temperatures, making them well-suited for next-generation processing techniques where high fluxes of low energy ions are desirable. In this work, we focus on plasma generation in fluorine containing gas backgrounds due to their relevance to a number of industrial plasma applications. In particular, we focus on the effect of fluorine-containing gas dilution on the plasma properties of electron beam generated plasmas including electron density, total plasma density, electronegativity, and electron temperature. These parameters are measured through a combination of Langmuir probe, and RF impedance spectroscopy techniques.

6:00pm **PS-WeA12 Characterization of Hydrogen Recombination at the Wall and its Effect on Hydrogen Source Performance**, *Shaun Smith*, MKS Instruments, Inc.

There is ongoing interest in using remote plasma sources for on wafer processing with hydrogen radical based chemistries. Yet there has been limited availability of reliable measurements for recombination rates, as they pertain to semiconductor processing. Presented here are diagnostics and some insight to understating of how process responds to material choice or the surface condition of the plasma facing wall. The impact that surface recombination of radical species has on the discharge is discussed and the impact that surface material choice and condition has on source operation and process performance is examined. As well as a discussion of factors that can effect that recombination rate. These parameters are explored in the 1-10torr 1-5slm and 1-10kW regime

Atomic hydrogen recombination rate is measured for a range of materials. Toroidal plasma sources are then built with these materials as the plasma facing wall and are characterized for their discharge parameters and atomic hydrogen output. The discussion will include a description of the diagnostic tools used in this study; a comparison of modeled source discharge parameters running in Ar and H2 with experiment along with a brief comparison of the impact of volumetric and surface recombination of radical species is presented.

This work was specifically targeted for the use of radicals produced by a toroidal remote plasma sources for semiconductor applications but is generalizable to discharges in hydrogen independent of excitation or application.

Surface recombination of the hydrogen radical is shown to be a dominant mechanism in determining process parameters for semiconductor applications.

Manufacturing Science and Technology
Room: 302 - Session MS+PS+TF-ThM

Processes for Mesoscale Structure on Paper and Textiles
Moderator: Jesse Jur, North Carolina State University

8:00am MS+PS+TF-ThM1 High-Performance Composites Based on Wood Cellulose Nanofibrils, *Qi Zhou*, KTH Royal Institute of Technology, Sweden **INVITED**
With increasing concerns for the climate and environment, it has been recognized globally that paradigm-shifting research is required to improve the performance of materials based on renewable resources. Attempts to develop very high performance natural cellulosic fibers based composite materials using intact cells from hemp, flax and cotton have failed mainly due to the inherent imperfections of the secondary cell walls of natural fiber cells. These issues have been recently addressed by replacing with cellulose nanofibrils (CNFs), which are three orders of magnitude smaller than the intact fiber cells. The extraction process of CNFs from renewable resource has been extensively investigated in the past decade. A critical challenge in the fabrication of high performance products based on CNFs is to tailor their surface structure and functionality in an efficient and environmentally friendly fashion, thus to accommodate a wider range of applications and sustainability requirements for the next generation of materials. In this talk, I will present our recent work on the fabrication of functional composite materials based on CNFs. In particular, several novel surface modification techniques of CNFs and their effects on nanostructure and material properties of CNFs based composites will be discussed.

8:40am MS+PS+TF-ThM3 Manufacturing and Applications of Carbon Nanotube Textiles, *Philip Bradford*, North Carolina State University **INVITED**
Carbon nanotubes (CNTs) are short nanofibers that are usually produced in the form of a black powder. This powder is then incorporated into other materials to produce a wide array of multifunctional products. Processing raw CNTs into materials that look and behave like traditional textiles is a growing area of interest, however the CNTs are often processed in solution and the end products look more like papers than textiles. There are currently only a couple of options for creating fabrics out of CNTs which preserve the high surface area of the individual tubes and retain high porosity. This presentation covers the work of my research group to make this type of fabric from a special type of CNT structure called drawable CNT arrays. These arrays are synthesized in a low pressure chemical vapor deposition process and then utilized for CNT nonwoven fabric formation. My group is also exploring many novel applications for the use of these unique fabrics.

The nonwoven CNT fabrics produced in our lab contain millimeter long CNTs, have a preferential CNT alignment, low CNT bundling and high porosity. These features make them attractive for use in: composites reinforcement, battery electrodes, sensing, filtration and barrier fabrics. Of particular interest to the AVS community may be our recent work with collaborator Dr. Jesse Jur at NC State, to study the atomic layer deposition (ALD) of thin inorganic layers into CNT arrays and fabrics. Through optimization of CNT pretreatment, ALD parameters and sample orientation, we have been able, for the first time, to uniformly coat CNT structures whose characteristic aspect ratios are extremely large. Due to the un-bundled nature of the CNT fabrics we have the ability to uniformly coat CNTs along their entire millimeter length, making for some very unique hybrid CNT structures.

9:20am MS+PS+TF-ThM5 Carbonized Cellulose Fibers for Low-Cost Energy Storage, *Fei Shen*, *L.B. Hu*, University of Maryland, College Park
A low-cost but scalable carbon film was successfully obtained via cellulose fiber carbonization. This cellulose derived film can be also applied as an alternative anode for lithium or sodium ion battery due to its natural mesoporous structure of the starting material which was excellent for ion storage. Furthermore, this new type of carbonized cellulose possesses electrically interconnected three-dimensional framework with advanced dual properties of anode material and current collector, afford to result in a higher energy density by eliminating the extra mass of inactive materials such as binder and carbon black in conventional designs. Electrochemical studies showed the film achieved a high capacity of 800mAh/g for lithium ion battery and a moderate capacity of 200mAh/g for sodium ion battery at C/10.

9:40am MS+PS+TF-ThM6 Traditional, 20th, and 21st Century Strengthening Techniques for Cultural Heritage Papers Weakened by Cellulose Depolymerization, *L. Pei, M. McGath*, *John Baty*, Johns Hopkins University
Cellulose depolymerization leading to paper brittleness can occur throughout the sheet, or be localized to where a corrosive substance is present. Uniform brittleness is associated with mass-produced, inexpensive, and acidic papers. Rendering millions of books and unbound papers useless, paper brittleness impairs scholarly communication and destroys historic and artistic works. Localized brittleness is most commonly associated with corrosive pigments and inks, including iron gall ink. It visually alters and can also physically destroy paper-based works. In the absence of techniques to restore the cellulose polymer to its initial condition, diverse techniques have been developed to strengthen paper. Traditional conservation techniques vary from conceptually simple ones, such as backing the sheet with a reinforcing layer, to complex ones, such as splitting the sheet into two plies to adhere a reinforcing sheet in-between. 20th century techniques include the widespread lamination of documents with a cellulose acetate film, the present condition of which we have studied and discuss along with its successor, the encapsulation of papers within a polyester film envelope to which the sheet is only electrostatically attracted. Both of these techniques involve the addition of a visible film, altering the look and feel of the artifact. Therefore, we are studying chemical vapor deposition (CVD) using Parylene to deposit a thin, conformal, barely perceptible coating to add strength to brittle papers. We conclude that, here as elsewhere, scientific research can improve traditional conservation techniques by making additional tools available to the conservator; that both cellulose acetate lamination and polyester film encapsulation have achieved a greater preservation benefit than they are credited for; and that CVD is a useful tool for both single-item as well as batch treatments to preserve cultural heritage papers weakened by cellulose depolymerization.

11:00am MS+PS+TF-ThM10 Visualizing the Interface in Strained Cellulosic Nanocomposites, *Chelsea Davis*, *J. Woodcock, A.M. Forster, M. Zammarano, I. Sacui, N. Chen, SJ. Stranick, J.W. Gilman*, National Institute of Standards and Technology (NIST)
In fundamental composite theory, the nature of the interface is often the key parameter which determines the strength of the resulting composite structure. While it is possible to observe interfacial failure and characterize the areal coverage of the matrix on the surface of the reinforcement phase in conventional composite materials, directly quantifying interfacial strength and contact area in a nanocomposite becomes far more difficult. A novel solution developed at NIST has been to utilize Förster resonance energy transfer (FRET) imaging[1,2] by preferentially labeling the interface within a nanocomposite system, allowing direct imaging of the interface with an optical microscope.[3] Zammarano et al. have shown that the incorporation of a FRET dye pair onto the surface of a cellulosic nanoreinforcement phase (dye 1) and within a polymer matrix (dye 2) allows visualization of the nanoscopic interphase region as the two dyes transfer energy on the same scale as the interphase depth (1 nm-100 nm).[3,4]

Building upon this FRET-based interfacial characterization technique, our goal is to develop a globally nondestructive measurement system that allows the quantitative characterization of key interfacial properties; first, the wetting and surface contact formed between the nanocellulose and an epoxy matrix and second, the deformation of the interface on the nanoscale upon application of small mechanical strains. We are constructing a suite of mechanical strain tools to enable *in situ* mechanical interrogation with simultaneous FRET imaging. The development of the first of these tools, uniaxial tensile test will allow a preliminary observation of small strain effects on the interphase region regarding the fluorescent response of the FRET dye pair. As a first proof of concept, it has been shown that FRET can be used to observe nanoscopic interfacial fracture and to determine local (microscopic) stress concentration zones before macroscopic failure of the nanocomposite is observed.

This *in situ* FRET/mechanical deformation approach allows the use of an optical microscope to probe nanoscale features in a powerful way, enabling characterization of nanomaterials which will complement measurements made by electron microscopy and standard mechanical property testing methods.

Topic Area: Novel nanocomposites, Multi-technique characterization of nanostructured materials

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11:20am MS+PS+TF-ThM11 SERS-based Chemical and Biological Analytics on Inkjet-fabricated Paper Devices, *Ian White*, University of Maryland
SERS-based chemical and biological analytics on inkjet-fabricated paper devices

Abstract. As a bio/chemical sensing technique, surface enhanced Raman spectroscopy (SERS) offers sensitivity comparable to that of fluorescence detection while providing highly specific information about the analyte. The high sensitivity of SERS detection results from the localized plasmons generated at the surface of noble metal nanostructures upon excitation by resonant electric fields at optical frequencies. Although single molecule identification with SERS was demonstrated over a decade ago, today a need exists to develop practical solutions for point-of-sample and point-of-care SERS systems. Recently, we demonstrated the fabrication of SERS substrates by inkjet printing silver and gold nanostructures onto paper and other similar membranes. Using a low-cost commercial inkjet printer, we deposited silver nanoparticles with micro-scale precision to form SERS-active biosensors. Using these devices, we have been able to achieve detection limits comparable to conventional nanofabricated substrates. Furthermore, we have leveraged the fluidic properties of paper to enhance the performance of the SERS devices while also enabling unprecedented ease of use, which is critical for extending chemical and biological analytics from central labs out into the field.

In this presentation we will review the capabilities of inkjet-fabricated paper SERS devices as chemical and biological sensors. We will introduce the fabrication of paper-based fluidic SERS devices using inkjet printing, and we will review results for chemical detection with paper SERS devices, including the use of the paper substrates as swabs and dipsticks for pesticide detection, as well as chromatography SERS on PVDF membranes for the detection of melamine in infant formula. We will then present the results of the fluidic paper SERS devices for biomolecule detection, including paper SERS dipsticks that leverage the chromatographic separation properties of paper to distinguish the outcome of multiplexed TaqMan PCR from a single reaction. In particular, we have utilized this technique to detect the presence of two drug resistance biomarkers for methicillin-resistant *S. Aureus* (MRSA).

11:40am MS+PS+TF-ThM12 NSF Scalable Nanomanufacturing (SNM) Program, *Khershed P. Cooper*   **INVITED**
Abstract: Nanomanufacturing involves the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures such as nanodevices and nanosystems, and the integration of these into larger scale structures and systems such that both heterogeneity and complexity are possible with manipulation and control at nano-scale. In 2010, following a review of the NNI, PCAST recommended greater emphasis be put on commercialization of nanotechnologies by doubling Federal Government investment in nanomanufacturing R&D. In 2011, the inter-Agency NNI Signature Initiative (NSI) in Sustainable Nanomanufacturing was announced. In response to the NSI, the NSF Scalable Nanomanufacturing (SNM) Program was launched. SNM's emphasis is on research to overcome the key scientific and technological barriers that prevent the production of useful nanomaterials, nanostructures, devices and systems at an industrially relevant scale, reliably, and at low cost and within environmental, health and safety guidelines. The SNM program's objective is to address challenges presented at the various stages of the nanomanufacturing value chain of nano-scale building-blocks to nano-enabled products. It sponsors fundamental scientific research in well-defined technical areas that are strongly justified as approaches to overcome critical barriers to scale-up and integration. It seeks discovery of scalable processes and methods for large-area or continuous manufacturing at the nano-scale. It encourages the study of design principles for production systems leading to nanomanufacturing platforms, identification of metrology, instrumentation, and standards, and development of methodologies needed for process control and assessing quality and yield. SNM encourages an inter-disciplinary approach, industry collaboration and integration of research and education. SNM projects are studying a variety of building-blocks—CNT, graphene, membranes, BCPs, DNA, nanowires, nanofibers, QDs, etc., a variety of top-down and bottom-up processes—thermal, vapor-based, solution-based, lithography, patterning, bio-inspired, etc., targeting applications across the board—energy, environmental, electronics, sensors, structural, etc. Many projects are investigating roll-to-roll processing systems, some are studying in-line metrology and quality control. Moving ahead, SNM seeks to explore new research opportunities in processing (hierarchical nanomanufacturing, cyber-enabled nanomanufacturing, etc.), in materials (graphene, MoS2, etc.), in devices (plasmonics, ultrafine vias, etc.), and in manufacturing platforms (3D printing, bio-enabled assembly, etc.). SNM encourages an inter-disciplinary approach involving the disciplines of engineering, physical sciences and

mathematics. The ultimate goal is to create a knowledge base for the reliable production of nano-enabled systems and products.

Plasma Science and Technology
Room: 305 - Session PS1+TF-ThM

Plasma Deposition and Plasma Assisted ALD
Moderator: Sumit Agarwal, Colorado School of Mines

8:00am PS1+TF-ThM1 Sputtering Growth of High-Quality ZnO-based Semiconductors for Optoelectronic Applications, *Naho Itagaki*, Kyushu University, Japan   **INVITED**
ZnO and its related semiconductors are remarkable multi-functional materials with a huge range of existing and emerging applications including transparent conducting oxides (TCO) and light emitting diodes (LED). In order to obtain physical properties required for such applications, control of the crystallinity (grain size, crystal axis alignment, crystal defects) is of great importance. We have recently developed a new fabrication method based on magnetron sputtering, "Impurity mediated crystallization (IMC)", where crystal nucleation and the growth are controlled by impurity atoms adsorbed on the film surface [1,2]. Here we demonstrate sputtering deposition of two kinds of ZnO films by utilizing buffer layers fabricated via IMC method. One is polycrystalline TCO films fabricated on glass substrates, and the other is single crystalline films on sapphire substrates for LED applications. Effects of impurity during the crystal growth of ZnO are studied by observing the evolution of film morphology by means of atomic force microscopy (AFM).

IMC-ZnO buffer layers have enabled fabrication of single-crystalline ZnO films even on large lattice-mismatched (18%) sapphire substrates by a conventional sputtering method. The ZnO films have atomically-flat surfaces with steps of 0.26nm-hight, corresponding to a half of c-axis length of ZnO. AFM observation of IMC-ZnO buffer layers revealed that impurity atoms inhibit the crystal growth and thus increase in the grain density, which reduce the strain energy caused by the large lattice mismatch between ZnO and sapphire. IMC-ZnO buffer layers have also improved the film quality of ZnO based TCO fabricated on glass substrates. The most remarkable effect is a reduction in the resistivity of the films thinner than 100 nm. The resistivity of ZnO:Al films fabricated by conventional sputtering increases substantially from 6.3×10^{-4} W×cm to 1.5×10^{-3} W×cm with decreasing the film thickness from 100 nm to 20 nm, while the resistivity of ZnO:Al films with IMC buffer layers is low of $2.8\text{-}3.2\times10^{-4}$ W×cm in the thickness range 20-100 nm. The role of impurity here is to suppress the nucleation and allow the crystal growth with larger grains from the very early stage of deposition.

We believe that IMC method will not only accelerate the commercialization of ZnO in optoelectronic devices but also open up a new pathway for development of other oxide semiconductors, some examples of which including In_2O_3:Sn will be presented at the conference.

[1] N. Itagaki, et al., Appl. Phys. Express 4 (2011) 011101. [2] K. Kuwahara, et al., Thin Solid Films 520 (2012) 4507.

8:40am PS1+TF-ThM3 Novel Composite Materials Fabricated by Plasma-enhanced CVD of Carboranes and Pyridine or Benzene, *Robinson James*, *U. Chiluwal*, University of North Texas, *E. Echeverria*, University of Nebraska-Lincoln, *R. Gapfizi*, *J. Tae*, University of North Texas, *P.A. Dowben*, University of Nebraska-Lincoln, *J.A. Kelber*, University of North Texas
Altering the electronic structure of carborane-derived boron carbides by incorporating aromatic compounds is of scientific and technological interest in neutron detection and microelectronics. The fabrication of novel composite materials derived from ortho-carborane or meta-carborane with benzene or pyridine by plasma enhanced chemical vapor deposition (PECVD) at room temperature may lead to improved device performance over conventional boron carbides. The chemical composition and electronic structure of the resulting films were studied using in-situ x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) respectively. XPS of composite films of carboranes with pyridine shows the evidence of B-N bond formation during the PECVD process. Pyridine incorporation in the boron carbide materials resulted in the improved adhesion of physical vapor deposited Cu (PVD Cu) overlayers on the surface. XPS indicates that no thermal induced diffusion/dewetting of Cu was observed in the ortho-carborane and pyridine composite films even after annealing up to 1000K in UHV. In contrast, pure boron carbide films exhibited poor adhesion of Cu overlayers on the surface resulted in the significant dewetting during 400-

600 K annealing although no diffusion of Cu was observed even after annealing up to 1000 K. Composite films of ortho-carborane or meta-carborane with benzene were also grown on Si substrates by PECVD. These carborane: benzene composite films exhibit augmented B-C bond formation due to linking of benzene with the icosahedral carborane units as evidenced by XPS.

9:00am PS1+TF-ThM4 Engineering High-k Dielectric Gate Stacks using *In Situ* Spectroscopic Ellipsometry, *Yuanxia Zheng*, Penn State University, *G.B. Rayner*, Kurt J. Lesker Company, *A. Agrawal, S. Datta, R. Engel-Herbert*, Penn State University

The development of Ge-based field effect devices requires the integration of a high quality dielectric that forms an electrically well behaved semiconductor dielectric interface. Although GeO_2/Ge has been found promising, the thermodynamic instability as well as the relatively low dielectric constant of GeO_2 requires an alternative approach. The utilization of an ultrathin Si layer to move the semiconductor/dielectric interface from Ge into Si has been successfully demonstrated; however, the introduction of a planar thin layer into the gate stack is incompatible with a 3D FinFET manufacturing process flow. It is thus desirable to develop a multilayer gate stack by atomic layer deposition process, where an ultrathin GeO_2 layer can be thermodynamically stabilized and combined with a high-k dielectric film to meet the stringent requirement of low interface trap density and large capacitance density while maintaining a low gate leakage.

In this talk, we will present an approach of developing a multilayer gate-stack of HfO_2/Al_2O_3/GeO_2 for Ge using in-situ processing control in plasma-enhanced atomic layer deposition (PEALD) by utilizing real-time monitoring capabilities of in-situ spectroscopic ellipsometry (SE). Pristine Ge-surface is obtained by removing native GeO_x using H-plasma and an ultrathin GeO_2 layer is grown thereafter by O-plasma anneal; in-situ SE is used to monitor the process and to control GeO_2 thickness. An ultrathin bilayer of alumina and hafnia is subsequently grown using thermal ALD and large capacitance densities with equivalent oxide thicknesses (EOT) below 1 nm and gate leakages below $1 \times 10^{-4} A/cm^2$ at -1V (EOT=0.7 nm) are demonstrated. The impact of the thickness of the individual dielectric layers on interface trap density, determined by the conductance and the Terman method, leakage current and EOT is discussed. We will further discuss how in-situ SE is used to optimize process-relevant parameters for native oxide etching, intentional oxidation and deposition of high-k dielectrics. The potential of this in-situ real-time process metrology is projected for the development of high quality high-k dielectrics on other high mobility low band gap semiconductor materials.

9:20am PS1+TF-ThM5 Impact of Low Frequency Addition to RF Power in PECVD Process: Case of TiN and GeTe, *Christophe Vallee*, *F. Piallat, M. Aoukar, P.D. Szkutnik*, LTM - CEA/LETI, France, *R. Gassilloud, P. Noé, P. Michallon*, CEA, LETI, MINATEC Campus, France

In Dual Frequency plasma etching, one frequency is chosen to be much higher than the other in order to achieve an independent control of ion bombardment and electron density (i.e. ion flux). It is assumed that high frequency control the density and low frequency (LF) the energy. Recently, many groups have simulated the effect of LF addition to RF source. Depending on the model, it has been reported that the plasma density may be reduced due to sheath width variation as well as it may be increased due to highly energetic secondary electrons. Donko *et al* have shown how the γ coefficient of the secondary electrons may be used to interpret contradictory published papers [1] and they concluded that there is only a small pressure process window for which the effect of secondary electrons on the ionization compensates the effect of the frequency coupling.

The interest of adding LF to RF plasma in order to enhance the deposition reaction mechanisms is demonstrated here. An in depth investigation of plasma by Optical Emission Spectroscopy shows that the plasma density increases when adding LF (350 Khz) in a RF (13.56 Mhz) metal deposition process. In this case, the plasma enters a γ-mode due to secondary electron heating. This mode is not obtained when depositing semiconductors (GeTe) or dielectric, i.e. depending on the biased nature of the surface of showerhead electrode during the process. Adding LF to RF also modifies the sheath thickness of the plasma and increases the electron temperature of the gas [2]. In our experiments, all the deposited materials show different properties and new emission peaks are observed by OES for all precursors. Carbon content, density and growth rate are strongly modified by adding LF. For example, in case of TiN we found that the deposition rate is increased by a factor of two while in the same time the resistiviy is strongly reduced (50%) and the density is going from 3.4 to 3.8 $g.cm^{-3}$[3]. We also studied the plasma impact on the Equivalent Oxide Thickness (OET) regrowth of a TiN/HfO_2 integrated MOS capacitors. For phase change material (PCM) applications, very different cycles (amorphous to crystalline) are observed for devices with RF GeTe or LF+RF GeTe. All the deposition processes are performed in 200 (GeTe) and 300 mm (TiN)

pulsed liquid injection PEMOCVD chambers from AltaCVD Advanced Materials™, located in CEA-LETI cleanroom.

[1] Z. Donkó, *et al*, Appl. Phys. Lett. **97** (2010) 081501

[2] W-J Huang *et al*, Phys. Plasmas **16** (2009) 043509

[3] F. Piallat *et al*, *J. Phys. D: Appl. Phys.***47** (2014) 185201

11:00am PS1+TF-ThM10 Surface Reactions during Ammonia-Plasma-Assisted Atomic Layer Deposition of Silicon Nitride, *Dennis Hausmann*, Lam Research Corporation, *R. Ovanesyan, S. Agarwal*, Colorado School of Mines

The advent of FinFETs with high-aspect-ratio 3-D geometries increases demands on conformality of the SiN_x films. These stringent requirements on conformality and low thermal budget can be simultaneously met using atomic layer deposition (ALD). While there are a few reports in the literature that show that SiN_x can be conformally deposited via ALD at <400 °C, these films are not sufficiently dense to serve as moisture or oxidation barriers. Hence, improvements in this area are needed via a fundamental understanding of the surface reaction processes. Recently, we have developed a novel ALD processes for the growth of Si_3N_4 thin films using trisilylamine ($Si(NH_3)_3$, TSA) and silane precursors, and an NH_3 plasma. This ALD process with TSA provides dense films with a conformal coverage over aspect ratios typical for the applications; 10:1. To understand the underlying film growth mechanism, the specific surface reactions involved during each half-reaction cycle of this ALD process were monitored with *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. ZnSe internal reflection crystals were used as substrates since ZnSe is transparent in the infrared up to 700 cm^{-1}. This spectral range, combined with the high sensitivity achieved with ATR-FTIR spectroscopy, allows us to identify and monitor in real time the different surface species generated and consumed due to sequential exposure of the growth surface to Si-containing precursors and an NH_3 plasma. The vibrational modes that were monitored include the surface SiH_x and NH_x stretching modes in the 2100 and 3400 cm^{-1} region, respectively, and Si_3N_4 phonon modes, which appear in the 800-900 cm^{-1} region. The corresponding surface reaction products were monitored using quadrupole mass spectrometry. Further, these films were extensively characterized using a suite of *ex situ* diagnostic tools.

11:20am PS1+TF-ThM11 Plasma Assisted Atomic Layer Epitaxy of III-N Ternaries for Next Generation Devices, *Neeraj Nepal*, *J.K. Hite, V.R. Anderson, V.D. Wheeler, S. Qadri, C.R. Eddy*, Naval Research Laboratory

III-Ns (InN GaN and AlN) and their alloys have been attractive semiconductor materials for application in a wide range of device technologies. The most common growth methods of this material system are CVD and MBE, but these conventional growth techniques have challenges in achieving alloys without phase separation over the entire stoichiometric range, ultimate thickness control at the atomic level, and the ability for *in situ* growth of complete device structures. Plasma-assisted atomic layer epitaxy (PA-ALE) is a promising method to grow III-N alloys and incorporate them into device structures as it allows low temperature growth and precise control of thickness, stoichiometry and uniformity. Recently, PA-ALE has been used for the growth of III-N binaries at low temperatures (≤500°C)[1,2]. Ternary growth at these low temperatures could eliminate miscibility gaps, which has been an issue for conventional growth methods.

We present the growth and characterization of III-nitride ternaries by PA-ALE over a wide stoichiometric range including the range where phase separation has been an issue for MBE and CVD. Using our previously reported optimal growth conditions for GaN, InN [1], and AlN [2], $Al_xGa_{1-x}N$, $In_xAl_{1-x}N$ and $In_xGa_{1-x}N$ (0≤x≤1) alloys were grown at 250–500 °C. Group III-B metal contents in these alloys were varied with binary cycle ratios and the alloy compositions were determined by XPS and XRD and reflectivity measurements. Since the growth rate (GR) of InN is slower than that of AlN, a digital alloy produced from 3 cycles of InN for every cycle of AlN results in an $Al_{0.83}In_{0.17}N$ film. The GaN GR, however, is slower than InN, and $In_{0.54}Ga_{0.46}N$ alloy was grown for every alternating cycle of GaN and InN. Additionally, 4 cycles of GaN for every cycle of AlN gave $Al_{0.5}Ga_{0.5}N$ alloy and the measured concentration was confirmed optically. By this digital alloy growth method, we are able to grow In containing ternaries by PA-ALE in the spinodal decomposition region (15-85%). The surface roughness of III-N alloys on GaN were the same as the starting roughness of 0.4 nm. Optimal ternary growth conditions were used to synthesize III-N based device structures on GaN and demonstrated 2DEG at the interface. We will present electrical and optical data on ALE III-N heterojunctions on GaN templates.

These early efforts suggest great promise of PA-ALE for addressing miscibility gaps issue encountered with conventional growth methods and realizing high performance optoelectronic and electronics devices involving ternary/binary heterojunctions, which are not currently possible.

[1] N. Nepal et al., JCGS **13,**1485 (2013).

[2] N. Nepal et al., APL **103**, **0**82110 (2013).

11:40am PS1+TF-ThM12 Plasma-enhanced Atomic Layer Deposition: Prospects and Challenges*, Hyungjun Kim*, Yonsei University, Korea **INVITED**

Due to various benefits such as atomic level thickness control and excellent conformality, atomic layer deposition (ALD) is expected to play an important role in future device fabrication. Especially, plasma enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than conventional thermal ALD. This low temperature process makes PE-ALD more attractive for emerging nanoscale device fabrication. In addition, since ALD is surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. In this presentation, the basic characteristics and several examples of PE-ALD processes for various applications such as semiconductor/display devices fabrication will be presented. The PE-ALD is a valuable tool to deposit very thin metal layers with good properties including little nucleation delay and high purity. Co, Ni, Ru films with good conformality was deposited by PE-ALD using NH3 plasma. Film properties as well as applications for emerging electronic devices of the metal PE-ALD will be discussed. Also, the use of plasma for ALD enables improvements in electrical properties of next generation semiconductor devices. Various high k oxides including HfO2, CeO2, La2O3 and doped high k oxides were deposited by PE-ALD from metal organic precursors and oxygen plasma. Especially, comparative study between PE-ALD and thermal ALD has shown that the interface defect density and leakage current are better for PE-ALD. Also, PE-ALD of ZnO thin films was investigated for thin film transistors. We studied the modulation of device parameters of PE-ALD ZnO based TFTs using UV light exposure. Finally, PE-ALD TiO2 thin films have shown high photocatalytic effects on various substrates. These indicate that the PE-ALD processes are versatile methods enabling nano scale manufacturing in emerging applications.

Plasma Science and Technology
Room: 308 - Session PS2+TF-ThM

Atomic Layer Etching (ALE) and Low-Damage Processing

Moderator: Geun Young Yeom, Sungkyunkwan University, Republic of Korea

8:00am PS2+TF-ThM1 Fluorocarbon Assisted Atomic Layer Etching of SiO$_2$ and Selectivity over Si Using Cyclic Ar/C$_4$F$_8$ Plasma*, Dominik Metzler**, University of Maryland, College Park*, S.U. Engelmann, R.L. Bruce, E.A. Joseph*, IBM T.J. Watson Research Center*, V.A. Godyak*, University of Michigan*, G.S. Oehrlein*, University of Maryland, College Park

There is great interest in establishing directional etching methods capable of atomic scale resolution for fabrication of highly scaled electronic devices. Recently, controlled etching of SiO$_2$ at the Angstrom-level based on steady-state Ar plasma, periodic injection of a defined number of C$_4$F$_8$ molecules, and synchronized plasma-based Ar$^+$ ion bombardment has been shown [1]. Controlled etching is based on deposition of a thin (~ several Å) reactive fluorocarbon (FC) layer on SiO$_2$ enabled by precise C$_4$F$_8$ injection. For low energy Ar$^+$ ion bombardment conditions, the physical sputter rate of SiO$_2$ vanishes, whereas SiO$_2$ can be etched when FC reactants are present at the surface. In this work, plasma conditions have been characterized in real time during cyclic exposure using a Langmuir probe. Changes in plasma potential, electron density, and electron temperature are measured throughout each cycle and compared to continuous precursor addition. Continuous precursor addition has a higher C$_4$F$_8$ concentration than periodic injection. The C$_4$F$_8$ injection has a short, significant impact on the plasma properties within each cycle and a small impact for longer time scales, i.e. from cycle to cycle. Observed trends in plasma properties agree with continuous precursor addition. Additionally, this cyclic approach was used to investigate the transition from SiO$_2$ to Si etching employing SiO$_2$-Si-SiO$_2$ layers. Si etching and the selectivity of SiO$_2$ over Si is investigated as a function of FC surface coverage, ion energy (20 to 30 eV), and etch step length using *in situ* ellipsometry. Time-dependent etch and deposition rates are compared for Si and SiO$_2$. The etch behavior during the cyclic approach is compared to continuous precursor addition etching of SiO$_2$ and Si. X-ray

photoelectron spectroscopy is used to investigate surface chemistry at various stages of the cyclic etching and will be reported.

References:
[1] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, J Vac Sci Technol A **32**, 020603 (2014)

8:20am PS2+TF-ThM2 Highly Selective Atomic Layer Etching of Silicon Dioxide Using Fluorocarbons*, Eric Hudson, V. Vidyarthi, R. Bhowmick, R. Bise, H.J. Shin, G. Delgadino, B. Jariwala, D. Lambert, S. Deshmukh*, Lam Research Corporation

As microelectronics advancements require smaller device features, masking layers are becoming thinner. Additionally, there are tighter requirements on allowable loss of films during processing. This leads to exacting requirements for etch, where a target film must be removed with very high selectivity to a mask and/or substrate film. For etching of SiO2 or similar materials, this high selectivity is typically achieved using very polymerizing fluorocarbon-based combinations of gases. However this approach can introduce problems with etch rate loading, such that the oxide in features with larger critical dimension (CD) tends to etch more slowly due to excessive passivation.

A novel approach for oxide etching has been developed which addresses this tradeoff between selectivity and etch rate loading. The etch process is based on repeated cycles of fluorocarbon deposition and etch reaction activation, similar to the process described by Metzler et al [1]. In each cycle there are two different phases of plasma conditions in which (1) a thin film of fluorocarbon polymer is deposited and (2) the polymer film is bombarded by noble gas ions to activate the etch reaction. Under the right conditions, oxide films are incrementally etched in each cycle. This atomic layer etch approach is less susceptible to etch rate loading because under properly adjusted conditions, the oxide etch front remains clear of polymer buildup after each cycle. Under the same conditions, polymer can build up on the mask or substrate surface with successive cycles, protecting the film and resulting in minimal loss. The process times for the deposition and activation phases of the cycle are the primary parameters for process control. A comparison of model and experiment is presented to characterize the effect of these two time parameters upon process results.

[1] Metzler, et al JVST A 32, 020603 (2014).

8:40am PS2+TF-ThM3 Electron Beam Plasma Tool for Atomic Precision Etching*, Leonid Dorf, S. Rauf, M.-F. Wu, Y. Zhang, F. Tavassoli, K. Ramaswamy, K. Collins*, Applied Materials Inc.

As the node size diminishes, microelectronics fabrication progressively requires atomic layer precision, so it becomes critical to accurately control ion energy during plasma processing. Damage caused by conventional plasma technologies (capacitively or inductively coupled plasmas) is becoming unacceptable for critical etch and clean applications. Using electron sheet beam parallel to the substrate surface to produce plasma in a processing chamber provides an order of magnitude reduction in electron temperature T_e (~ 0.3 eV) and ion energy E_i (< 2 eV without applied bias) compared to conventional plasma technologies, thus making electron beam plasmas an ideal candidate for processing features at 5 nm and below. In this presentation, we report processing results for a range of advanced plasma etching applications tested using the electron beam generated low T_e plasma. Using patterned wafers, we have developed low-bias power (0 – 10 W) processes resulting in infinite selectivity (as per high-resolution TEM images) of silicon nitride to silicon oxide and poly-silicon in fluorocarbon based chemistries. Such high selectivity can be attributed to the two phenomena: (1) at very low bias power, ion energy is sufficiently small to allow processing near the etch threshold, and (2) plasma ions and radicals in the electron beam generated plasma are produced by highly energetic (~ 2000 eV) electrons, such that the ratio between dissociation and ionization cross-sections for most gases differs considerably from that in conventional tools with chemical processes determined by 10-15 eV electrons. The latter results in weak dissociation of the fluorocarbon gas (CH$_2$F$_2$) and relatively low free fluorine concentration, which in turn leads to very low silicon etch rate. We have also investigated a nitride spacer application, in which 20 nm nitride layer deposited conformly over a silicon fin needs to be etched away to produce straight side walls for further double patterning (as one application). Our results indicate that using the electron beam plasma provides suitably small footing with a reasonably small slant angle of the shoulder, at the same time being selective to the underlying silicon layer. Accurate analysis of several time-series of TEM images allowed characterization of lateral and vertical etch processes over a range of operating conditions, such as the bias power and the beam current. Initial studies also indicate excellent loading characteristics, even at high bias

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* Coburn & Winters Student Award Finalist

power, which again can be attributed to unique chemical composition of the processing gas in the electron beam generated plasma.

9:00am PS2+TF-ThM4 Precise Theoretical Calculation of Neutral Beam Generation Efficiency by Collision of Chlorine Against Graphite Surface, *Tomohiro Kubota*, Tohoku University, Japan, *N. Watanabe, S. Ohtsuka, T. Iwasaki, K. Ono, Y. Iriye,* Mizuho Information & Research Institute, 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 (Cl_2^+) [2]. However, the mechanism has not been clarified. Recently we investigated the neutralization mechanism by using numerical simulations based on quantum mechanics [3] and succeeded in explaining higher neutralization efficiency of negative ions than positive ions.

In this study, collision process of a chlorine particle (Cl, Cl^-, Cl_2, or Cl_2^+) against graphite surface was simulated by calculation based on time-dependent density functional theory (TD-DFT). Neutralization efficiency was calculated from the number of the valence electrons on the particle after the collision. By using a unit cell with enough size, dispersion of electron density into vacuum was suppressed and quantitative interpretation became possible.

Also, dependence on incident angle and energy of the particle was investigated. It was found that experimental result of energy dependence of the neutralization efficiency was quantitatively reproduced by the calculation. It suggests we have achieved a precise simulation of the neutralization process.

A part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

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

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[5] T. Kubota et al., J. Phys. D: Appl. Phys. **45**, 095202 (2012).

9:20am PS2+TF-ThM5 Achieving One Tenth of a Nanometer Precision in Etching of SiO₂ Over Silicon: Challenges and Opportunities, *Gottlieb Oehrlein*, University of Maryland, College Park **INVITED**

We discuss use of low pressure plasma surface interaction mechanisms aimed at achieving atomic scale precision in etching materials. Using a steady-state Ar plasma in conjunction with periodic injection of a defined number of C_4F_8 molecules and synchronized plasma-based Ar^+ ion bombardment, we have shown that one tenth of a nanometer precision in etching of SiO_2 is possible.[1] For low energy Ar^+ ion bombardment conditions giving a maximum ion energy of about 20eV, the physical sputter rate of SiO_2 vanishes whereas for an FC-coated SiO_2 surface, chemical modifications of the SiO_2 surface take place and SiO_2 etching is initiated. Precise management of C_4F_8 supply enables control of the deposited fluorocarbon (FC) layer thickness in the 1 to several Ångstrom range. We will discuss the temporal variation of the chemically enhanced etch rate of SiO_2 for Ar^+ ion energies below 30 eV as a function of fluorocarbon surface coverage which enables controlled removal of Ångstrom-thick SiO_2 layers per process cycle. We will also discuss silicon underlayer etch rate measurements and challenges connected with this approach.

[1] D. Metzler, R. Bruce, S. Engelmann, E. A. Joseph, and G. S. Oehrlein, J Vac Sci Technol A **32**, 020603 (2014)

11:00am PS2+TF-ThM10 Numerical Simulation of Atomic Layer Etch via FPS3D, *Paul Moroz*, Tokyo Electron US Holdings

Atomic layer etching (ALE) and atomic layer deposition (ALD) are becoming more attractive processing methods primarily due to their higher control of profiles and less induced damage to materials. They require multi-step processing, with each time-step having its own chemistry, incoming fluxes, and energy distribution of species. In this work, we simulated ALE of Si by employing a cycle of two main steps: chlorination of Si surface layer by Cl2 gas and then removal of the chlorinated layer with Ar neutral beam of low energy and narrow energy spectrum, so the sputtering of Si could be neglected. Feature scale simulator FPS3D [1,2] is

well designed for the multi-step operations and allowed us to replicate main results of the corresponding experiments [3]. Each step in ALE processing was self-limiting, and we have used the same conditions and parameters as reported for the experiment. The intermediate gas-purge steps were excluded, as simulations allow instantaneous change of chemistry and fluxes, which is not possible in actual processing. We will demonstrate simulation of ALE processing with clear time resolution of chlorination and removal steps and with etch rate corresponding to experiments.

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[3] J.K. Kim, et al, J. Vac. Sci. Tech. A 31, 061310 (2013).

11:20am PS2+TF-ThM11 Low Damage Etch Residue Removal of CoFeB Material using CO/NH₃ Reactive Ion Beam for STT-MRAM Device, *MinHwan Jeon*, K.C. Yang, D.H. Yun, J.Y. Youn, G. Yeom, Sungkyunkwan University, Republic of Korea

Spin transfer torque magnetic random access memory (STT-MRAM) is a promising candidate for the next generation memory device due to high density, nonvolatile storage, fast switching speed, etc. comparing to conventional memory devices. For the nano scale STT-MRAM device fabrication, the dry etch process is one of the critical issues due to difficulty in the formation of volatile compounds between MTJ materials such as CoFeB, CoPt, MgO, NiFe and etch gases. The MTJ materials have been etched using conventional reactive ion etching (RIE) system with noncorrosive gases such as CO/NH_3, CH_3OH so as to increase the volatile compounds. However, the relatively low etch selectivity over hard mask material and etch residue still remain on the etched pattern sidewall. In this study, reactive ion beam etching (RIBE) system has been applied to effectively remove the etch residues remaining after the main etch of CoFeB material in the conventional ICP system. The CO/NH_3 gas mixtures was also used for the removal of the etch residues on the sidewall of etched MTJ features. After the optimized RIBE, the etch residue was effectively removed, the surface composition was restored, and the surface roughness of the etched CoFeB thin film after the etching in the RIBE system was decreased indicating the effective removal of redeposited etch residue by the RIBE. The other characteristics of CoFeB substrate after the residue removal by the RIBE were also investigated and will be reported in the presentation.

11:40am PS2+TF-ThM12 Effects of Cryogenic Cooling on Gallium Nitride Film in Argon Plasma, *Daisuke Ogawa*, Y. Nakano, K. Nakamura, Chubu University, Japan

We have developed the technique to reduce the damage that is induced by argon plasma to the surface of a gallium nitride (GaN) film. Our technique especially reduces the damage relating to the band gap more than 2.5 eV. Our in-situ monitoring showed that a GaN film cooled with liquid nitrogen (LN_2) has a different pattern of the damage induced by the plasma.

In order to make the in-situ monitoring of the GaN surface, we made real-time measurements with photoluminescence (PL) spectrum emitted from the GaN film. Here, the GaN film was excited with a light illumination generated from a xenon lamp passing through a 313 nm band pass filter. This configuration allows us to monitor the volume-averaged material condition from the surface to ~75 nm depth. M. Chen previously found that the ratio of the blue luminescence (BL) band over the near-band edge (NBE) band is effective to make the in-situ monitoring of the damage induced by plasma.[1] The ratio basically gets larger as the film gets more damages. However, our result showed that the ratio stayed almost constant only when the film was cooled with LN_2. This means that the damage induced by the argon plasma was likely avoided by using LN_2 cooling.

To find the effect of the cooling with LN_2, we made X-ray photoelectron spectroscopy (XPS) measurements for three samples (pristine, LN_2, and no LN_2) after the plasma exposures. We sputtered the film with argon ion beam for 3 minutes in vacuum every cycle of the XPS measurements to obta in the depth profile. The XPS spectrum from the GaN film that was exposed in argon plasma *with LN_2 cooling* was matched well with the spectrum from the pristine GaN film after the first sputtering. On the other hand, the XPS spectrum from the GaN film that was exposed in argon plasma *without LN_2 cooling* showed a chemical shift at the gallium line and a decrease at a nitrogen line. All three spectra matched well after the second sputtering. This profile indicates that the plasma-damaged layer thicker than ~30 nm was formed in the case of no LN_2 cooling. (Assumed the sputtering rate at 5 nm/min.)

Our in-situ temperature monitoring on the GaN surface that was exposed in the argon plasma showed that the temperature stayed below 150 ° C with LN_2 while the temperature exceeded over 300 ° C without LN_2. This is the indication that we should be able to reduce the damage by controlling the GaN film temperature during the plasma processing.

In this presentation, we will show the evolution of the PL spectrum, connecting with the surface temperature, XPS results supporting with more details.

[1] M. Chen et al., App. Phys. Let. 101, 071105 (2012)

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 315 - Session SM+AS+BI+PS-ThM

Plasma Processing of Antimicrobial Materials and Devices
Moderator: Heather Canavan, University of New Mexico, Morgan Hawker, Colorado State University

8:00am **SM+AS+BI+PS-ThM1 Plasma Polymers: Dogma, Characteristaion and Challenges**, *Sally McArthur*, Swinburne University of Technology, Australia **INVITED**
Plasma polymers, the dogma tells us are densly cross-linked, pinhole free films that adhere to virtually any dry surface. But when you are working at low power and trying to retain specific functional groups within your films, is this still true? How does environment (pH, salt concentration) effect film behaviour and what do respnses to change in environment tell us about the nature of these films? This talk will explore methods for studying the physicochemical behaviours of plasma polymer films and discuss how these films can be manipulated address specific biomaterials challenges.

8:40am **SM+AS+BI+PS-ThM3 The Role of Plasma Surface Modification in Antimicrobial Thin Films and Strategies**, *Renate Foerch*, FhG-ICT-IMM, Germany **INVITED**
"Delivery on demand" has become a key issue in the development of solutions for bacterial infection and the evolution of resistance. Antimicrobial bioactive coatings may be thin layers, scaffolds or hybrid materials with chemically immobilized or physically embedded antimicrobial substances that act while tethered to a surface or that are released either passively or upon a stimulus. Examples include burst release systems of an antimicrobial from plasma polymerised thin films that have fed into a recent efforts aiming to develop, characterize and evaluate nanocomposite coatings consisting of thin films, nanoparticles and nanocarrier systems. The nanocomposite coatings are formulated to respond to specific changes in the surrounding environment. The work to be described is part of a European-Australian effort to investigate new strategies to combat microbial infection; it draws expertise from plasma assisted technologies and wet chemical post plasma attachment of responsive nanocontainers carrying an antimicrobial to treat bacterial infection.

9:20am **SM+AS+BI+PS-ThM5 Plasma Modification of Drug-Eluting Materials for Localized Action at Medical Device Interfaces**, *J. Joslin, A. Pegalajar-Jurado, M.J. Hawker, E.R. Fisher, Melissa Reynolds*, Colorado State University **INVITED**
To direct protein and cellular behavior at the surface of synthetic materials, both localized chemical signaling and control over surface properties are required. To achieve requisite drug delivery dosages, hydrophobic polymers are often employed that slowly elute a therapeutic agent from the bulk material into systemic circulation. However, the surface free energy of the hydrophobic material can lead to deposition of undesired proteins and activation of the clotting. To overcome these challenges, advanced material platforms are needed to achieve localized therapeutic action and customizable surface properties. Herein, we present the development of $H_2O(v)$ plasma-treated PLGA-nitric oxide (NO) releasing materials. NO is a well-established anti-platelet and anti-microbial agent, and the NO release rate can be controlled by the hydrophobic nature of the bulk material where it was incorporated. Plasma treatment conditions were optimized to maintaining the NO release function while rendering the surface hydrophilicity. Despite the plasma conditions employed, the material retained 80-90% of the *S*-nitrosothiol content, while the NO release profiles were unaltered compared to the control. The change in the surface wettability was confirmed by water contact angle measurements. Extensive surface (XPS) and bulk (ATR FT-IR) chemical characterization demonstrated that the changes in wettability was due to the implantation of O-containing surface functional groups such as carbonyl and hydroxyl groups. In addition, optical profilometry analysis confirmed no statistically significant changes in the surface roughness compared to the control. Furthermore, the materials show minimal hydrophobic recovery after several days stored at -20°C. By combining both chemical signaling and

surface treatments into one material, we expect to reduce activation of clotting cascade and enhance the biocompatibility of the materials.

11:00am **SM+AS+BI+PS-ThM10 Plasma Treated Substrates Reduce Protein Adsorption**, *Marvin Mecwan, J. Stein, W. Ciridon*, University of Washington, *X. Dong*, Eli Lilly and Company, *B. Ratner*, University of Washington
Proteins irreversibly adsorb onto surface, causing losses from solution, denaturation, as well as aggregation. Hence, there have been recent efforts in the pharmaceutical industry to addressing the manufacture, packaging and delivery of protein-based pharmaceuticals. We propose the use of radio-frequency (RF) plasma deposition to create coatings on substrates relevant to the pharmaceutical industry—glass, stainless steel and cyclic olefin polymer (COP). The monomers of choice were acrylic acid (AA) and tetraglyme (TG) (hydrophilic), and perfluoropropylene (C3F6) and perfluoromethyl vinyl ether (C3F6O) (hydrophobic). All monomers were successfully plasma coated on all substrates, and did not delaminate as was determined from survey and detailed ESCA scans. Furthermore, no peaks associated with the substrates were seen in the scans, which indicate that the plasma coating are at least 100Å thick. Protein adsorption studies were carried out using 0.1mg/mL solution of I-125 tagged bovine IgG by adsorbing the tagged protein on the plasma treated substrates for an hour. All hydrophilic monomer plasma treated substrates had lesser protein adsorbed on their surfaces ($< 2ng/cm^2$) as compared to hydrophobic plasma treated substrates (10-14 ng/cm^2). This is in comparison to untreated controls that had 200-300 ng/cm^2 protein adsorbed on the surface. Furthermore, following ISO 10993-5 guidelines, by performing cytotoxic studies using NIH-3T3 fibroblasts all plasma treated substrates were determined to be non-cytotoxic. Hence, these results indicate that radio-frequency plasma treatment could lead to a new generation of surfaces that will be particularly effective for protein manufacture, storage and delivery. Future studies will be aimed at determining plasma coating thickness, protein aggregation assessment as well as studying the bonding strength of the proteins to the plasma treated surfaces.

11:20am **SM+AS+BI+PS-ThM11 Modification of Porous Materials by Low Temperature Plasma Treatment to Achieve Low-Fouling Membranes**, *Adoracion Pegalajar-Jurado, B.D. Tompkins, E.R. Fisher*, Colorado State University
Artificial porous polymeric membranes are used in many applications including water filtration systems and devices to treat blood for a broad variety of therapeutic purposes. In water filtration systems, membranes are used to remove colloidal particles and organic molecules from the watercourse and, in medical treatments, they function primarily to eliminate toxins from the blood before it is returned to the patient's body. Although these are very different applications, both are affected by membrane fouling from proteins, toxins, bacteria, and cells, which significantly decrease flow through the porous material. Surface modification techniques that retain the desired bulk properties are the ideal method for obtaining low-fouling membranes, thus extending their life-time in applications where they are exposed to fouling conditions. Here, we will present the properties of polysulfone ultrafiltration membranes subjected to H_2O plasma and their performance when exposed to proteins and bacteria. Plasma treated membranes showed enhanced hydrodynamic characteristics (i.e. increase in water flux) as a result of their high hydrophilicity. Notably, hydrophilic characteristics were retained for more than six months, ensuring top-shelf stability of the surface treatment. In terms of protein fouling performance, treated membranes show less bovine serum albumin adsorption than untreated membranes and cleaning of treated fouled membranes yields 70-90% flux recovery depending on plasma treatment time. This surface modification provides a mechanism for extending the life-time of the membranes.

11:40am **SM+AS+BI+PS-ThM12 Immobilized Laminin Concentration Gradients on Electrospun Fiber Scaffolds for Controlled Neurite Outgrowth**, *Nicole Zander*, US Army Research Laboratory, *T. Beebe Jr.*, University of Delaware
Neuronal process growth is guided by extrinsic environmental cues such as extracellular matrix proteins (ECM). Recent reports have described that the growth cone extension is superior across gradients of the ECM protein laminin compared to growth across uniformly distributed laminin. In this work, we have prepared gradients of laminin on aligned electrospun nanofibers for use as substrates for neuronal growth. The substrates therefore presented both topographical and chemical guidance cues. Step gradients were prepared by the controlled robotic immersion of plasma-treated polycaprolactone fibers reacted with N-hydroxysuccinimide into the protein solution. The gradients were analyzed using x-ray photoelectron spectroscopy and confocal laser scanning microscopy. Gradients with a dynamic range of protein concentrations were successfully generated and neurite outgrowth was evaluated using neuron-like PC12 cells. After 10

days of culture, PC12 neurite lengths varied from 32.7 ± 14.2 μm to 76.3 ± 9.1 μm across the protein concentration gradient. Neurite lengths at the highest concentration end of the gradient were significantly longer than neurite lengths observed for cells cultured on samples with uniform protein coverage. Gradients were prepared both in the fiber direction and transverse to the fiber direction. Neurites preferentially aligned with the fiber direction in both cases indicating that fiber alignment has a more dominant role in controlling neurite orientation, compared to the chemical gradient.

Thin Film
Room: 307 - Session TF+PS-ThM

Advanced CVD and Chemical Vapor Infiltration Methods
Moderator: Robert Davis, Brigham Young University

8:00am TF+PS-ThM1 Industrializing Single Wall Carbon Nanotubes by Water-Assisted CVD, *Don Futaba*, AIST, Japan **INVITED**
Since the discovery of the carbon nanotube (CNT) 20 years ago, extensive effort has been made to utilize their exceptional intrinsic properties toward industrial applications. However, availability has significantly thwarted these endeavors. In one section of my presentation, I will describe our efforts toward the economical mass-production of single-walled carbon nanotubes (SWCNT) based on the water-assisted chemical vapor deposition technique, from which highly efficient synthesis of vertically aligned SWCNTs grow from substrates (SWCNT forests). These SWCNT forests form through the self-assembly of individual SWCNTs when grown in sufficient density and have been shown to be useful templates for various applications from energy device electrodes to MEMS materials due both the continuous nature and high porosity. Further, I will describe the forest, and present a few examples of how we have infiltrated these material to create a new material with enhanced properties.

8:40am TF+PS-ThM3 Organoboranes as Single Precursors for Low Temperature CVD of Boron Carbide Thin Films for Neutron Detectors, *M. Imam,* Linköping University, Sweden*, C. Höglund,* European Spallation Source (ESS AB)*, J. Birch*, *Henrik Pedersen*, Linköping University, Sweden
The world-wide shortage of the ^{3}He isotope has led to a need for novel designs of neutron detectors. A detector based on the isotope ^{10}B, in the form of thin films, has been suggested by the European Spallation Source (ESS). The detector design uses ^{10}B$_4$C films, ≥1 μm, deposited on both sides of neutron transparent substrates such as Al blades.[1] The melting point of Al (660 °C) sets a strict upper temperature limit for CVD of the ^{10}B$_4$C films. Also, metallic Al will be badly affected by corrosive by-products, like HCl. This means that traditional B$_4$C CVD routes based on BCl$_3$ and CH$_4$ cannot be used. An alternative CVD route is to use oragnoboranes, i.e. molecules with direct B-C bonds, as such molecules are very reactive and do not produce corrosive by-products.

We have demonstrated the synthesis of thin, X-ray amorphous, boron-carbon films at low temperature (400-600 °C), by thermally activated CVD using triethylboron, B(C$_2$H$_5$)$_3$, (TEB) as single precursor on both single crystalline Si (100) and Al substrates.[2] Films with B/C-ratio of 4.6 with density 2.42 g/cm^3 (bulk B$_4$C density 2.52 g/cm^3) and 3.6 with density 2.14 g/cm^3 were deposited at 600 °C in hydrogen and argon ambient respectively, the impurity levels in the films was about 4 at.% of H at 600 °C. Further studies of TEB as precursor at higher temperatures (700-1200 °C) on Si substrates show that films with a B/C ratio of 4.5 and 3 were obtained from films deposited at 700 °C in hydrogen and argon ambient respectively with < 0.24 at.% of H. A threshold temperature of 1000 °C for the deposition is identified above which the B content decreases dramatically. Based on our results, a chemical mechanism for boron-carbon films from TEB, where the TEB molecule is decomposed to BH$_3$ and hydrocarbons, is suggested.

Plasma Enhanced CVD using trimethylboron, B(CH$_3$)$_3$, (TMB) is also explored to further lower the deposition temperature. Results from CVD and PECVD will be compared with state of the art PVD of ^{10}B$_4$C.

[1] R. Hall-Wilton et al. IEEE NSS/MIC conference record, 4283 (2012)

[2] H. Pedersen et al. *Chem. Vapor Deposition* 18, 221-224 (2012)

9:00am TF+PS-ThM4 High-Quality ZnO Thin Films Grown by a New CVD Method using Catalytically-generated High-energy Precursors, *T. Nakamura, Y. Ohashi, N. Yamaguchi, E. Nagatomi, T. Kato*, *Kanji Yasui*, Nagaoka University of Technology, Japan
ZnO is useful for many applications, and various growth techniques, including MBE [1-2], PLD [3, 4], and MOCVD [5], have been used to prepare ZnO films. Despite the advantages of MOCVD in industry, ZnO deposition by conventional MOCVD consumes a lot of electric power to react the source gases and raise the substrate temperature. To overcome this, a more efficient means of reacting oxygen and metalorganic source gases is needed.

In this paper, a new CVD method for ZnO film growth using the reaction between dimethylzinc (DMZn) and high-temperature H$_2$O produced by a catalytic reaction on Pt nanoparticles is presented [6]. H$_2$ and O$_2$ gases were admitted into a catalyst cell containing a Pt-dispersed ZrO$_2$ catalyst, whose temperature increased rapidly to over 1300 K due to the exothermic reaction of H$_2$ and O$_2$ on the catalyst. The resulting high-temperature H$_2$O molecules were ejected from a fine nozzle into the reaction zone and allowed to collide with DMZn ejected from another fine nozzle. ZnO epitaxial films were grown directly on a-plane sapphire substrates at substrate temperatures of 773-873 K with no buffer layer. Growth rates were 0.02-0.13 μm min^{-1}, and film thicknesses were 2-8 μm. X-ray diffraction patterns exhibited intense (0002) and (0004) peaks. The smallest FWHM value of the ω-rocking curve of ZnO(0002) was less than 0.1° (194 arcsec). The Hall mobility and residual carrier concentration of the epilayers were in the ranges 140-197 cm^{2}V^{-1}s^{-1} and 5.8×10^{16}-6.0×10^{17} cm^{-3} at 300K, respectively. This Hall mobility is very large compared with ZnO films grown directly on sapphire by other deposition methods. PL spectra at 10 K showed a strong emission peak at 3.360 eV, attributed to the neutral donor-bound exciton D^o_x. The FWHM was as low as 0.9 meV, which is smaller than that previously reported for ZnO obtained by MBE (5.5 meV) [4], and by PLD on a sapphire(0001) substrate (1.7 meV at 2K) [3]. .

[1] M. Sano et al., *Jpn. J. Appl. Phys.*, **42** (2003) L1050. [2] H. Tampo et al., *Appl. Phys. Lett.*, **84** (2004) 4412. [3] E. M. Kaidashev et al., *Appl. Phys. Lett.*, **82** (2003) 3901. [4] A. Ohtomo et al., *Semicond. Sci. Technol.*, **20** (2005) S1. [5] J. Dai et al., *J. Cryst. Growth*, **290** (2006) 426. [6] K. Yasui et al., *MRS Symp. Proc.*, **1494** (2013) 127

9:20am TF+PS-ThM5 Filling High Aspect Ratio Features: A Ballistic Transport Model, *Wenjiao Wang*, *J.R. Abelson*, University of Illinois at Urbana-Champaign
The ability to fill a high aspect ratio feature with a thin film material enables the fabrication of many nanoscale devices. Examples include shallow trench isolation or inter-metal dielectric in microelectronics. One approach is to use chemical vapor deposition under conformal coating conditions. However, as film builds up on the sidewalls the width of the feature shrinks and the aspect ratio increases sharply. This often results in incomplete filling, leaving a narrow void or 'seam' of low-density material along the central axis. One solution is to taper the feature into a 'V' shape, such that uniform deposition causes the apex of the V to move smoothly upwards.

To achieve complete filling, the flux of deposition precursor down the axis of the feature must be sufficient to maintain a uniform growth rate. Precursor transport is typically modeled using the diffusion equation under quasi-static conditions. We show that for high aspect ratio features, *the diffusion equation significantly under-estimates the flux of material that is deposited deep in the feature*. This occurs because the diffusion formalism assumes a mean transport distance between collisions that is proportional to the feature size. However, in molecular flow some of the transport events occur at glancing angles to the feature sidewall and afford very long flight paths. These events move precursor species to the bottom of the feature, an effect that enhances filling.

We have developed a ballistic transport model based on computing the emission/capture probability between all points on the surface and coding the result as a matrix. Species transport from a starting distribution is found by matrix multiplication to afford the distribution of final positions. We first show how the results of this model compare with the diffusion formalism: the bulk of the transport is similar, but the ballistic model predicts a 'tail' of long-range events. We then simulate the filling of V-shaped features as a function of the apex angle and sticking coefficient. The result is a prediction of regimes that can afford complete filling.

Finally, we consider the effect of growth rate saturation under high precursor flux, an effect that is physically significant and vastly improves conformal growth. We derive from the ballistic model the total flux arriving at each position, and self-consistently calculate the effective sticking probability. We simulate the coating profiles on rectangular and V-shaped features and determine that rate-saturated growth conditions, in combination with long-range precursor transport, greatly expand the regime that affords complete filling.

9:40am TF+PS-ThM6 Ozone Pretreatment's Effect on Infiltration of Carbon Nanotube Forests, *Richard Vanfleet, L. Barrett, J. Rowley, K. Hinton, R.C. Davis, D.D. Allred*, Brigham Young University

Thin films deposited on carbon nanotubes (CNTs) appear to be enabling materials for a variety of applications including: capacitive and electrochemical energy storage, chromatography and filtration chemical separations media, chemical sensing, and MEMS. Using CNT forests as a substrate creates new challenges to traditional thin film deposition techniques because of the need to penetrate into the forest and the chemical inertness of the CNT surface. We have explored the effect ozone pretreatment has on film morphology in two different deposition regimes: amorphous silicon deposited by low pressure chemical vapor deposition and nickel deposited by electroplating. TEM and SEM images of the forests after deposition show increased nucleation density on forests that were pretreated with ozone.

11:00am TF+PS-ThM10 A Novel Gap Fill Technology to Address the Current and Future Scaling Challenges of the Semiconductor Industry, *A. Mallick, Jingmei Liang, B. Underwood, K. Thadani, N. Ingle, T. Mandrekar*, Applied Materials Inc.

Gap fill has been a continuous challenge for the semiconductor industry driving innovation in the field of chemical vapor deposition. Applied Materials has continuously met this challenge by developing and refining CVD technologies to address the challenges of void-free gap fill in features of narrowing opening dimension and increasing aspect ratio. Technologies including Applied's HARP™ sub-atmospheric CVD and Ultima™ high density plasma established themselves as workhorses of the semiconductor industry. These technologies enabled dielectric materials including silicon dioxide, nitrides, carbides, and carbon in narrow gap. While these technologies see continued use in the manufacture of Logic and Memory device at <20nm node and below, gap fill of the narrowest and highest aspect ratio features required a new technical approach. As structure CD drops below 30nm, the sidewall angle approaches or exceeds 90° presenting a shape that promotes void or seam formation with conventional gap fill approaches including CVD and ALD.

To address these challenges Applied Materials has developed a new CVD technology we call FCVD™ to enable synthesis of high quality dielectric films including silicon oxides, silicon nitrides, silicon carbo-nitrides, silicon, low-k dielectrics, and carbon with a mechanism of film growth that promotes void-free fill irrespective of structure dimension and shape; this technology demonstrates capability to fill re-entrant structures with opening size <5nm and aspect ratio >20, flexibility to address multiple material systems and has been productized to address volume manufacturing requirements. In this paper we will demonstrate that we can achieve a void-free, profile-insensitive gap fill with multiple materials in a CVD reactor.

11:20am TF+PS-ThM11 Comparison of Carbonaceous Thin Films Deposited on Ru-capped Multilayer Mirrors via Extreme-Ultraviolet Light and Electrons, *Michael Barclay*, Johns Hopkins University, *N.S. Faradzhev, S.B. Hill, T.B. Lucatorto*, National Institute of Standards and Technology (NIST), *D.H. Fairbrother*, Johns Hopkins University

This presentation focuses on comparing growth characteristics of carbonaceous thin films produced by irradiation of Ru-capped multilayer surfaces with either extreme-ultraviolet light or electrons in the presence of hydrocarbon vapors. This work is motivated by the likelihood that extreme-ultraviolet lithography (EUVL) will be the next step in improving chip production for the semiconductor industry. Using a shorter (13.5 nm) wavelength of light, manufacturers can mass-produce microchips with feature sizes (< 10nm) that are impossible to achieve with current lithographic techniques. Since all materials strongly absorb 13.5 nm light, EUVL must be carried out under vacuum. Ultimately, this makes certain that the delicate multilayer optics and chemical photoresists, used in the EUVL process, cannot be completely isolated from one another. As a corollary, volatile organics released from resist-outgassing have the ability to be deposited via EUV- induced reactions, resulting in degradation of the multilayer optics. To protect the delicate optics, industry has established a resist-outgas testing protocol to determine the outgas-contamination risk of each resist before introducing it to the EUVL tool. This qualification procedure determines a resist's rate of contamination as well as the cleanability of its outgas products. Unfortunately, a key component of this protocol is the use of a dedicated, bright, EUV source. To mitigate the large capital investment necessary for such a source, electron beams are often used as a proxy. It is therefore important to correlate the carbon deposition processes induced by electron and EUV irradiation. To this end, we have exposed Ru-capped multilayer optics to both electron and EUV irradiation in the presence of admitted hydrocarbon vapors of two model species: benzene and tetradecane. Multiple exposures were performed with varying doses of EUV and electron irradiation for various hydrocarbon partial pressures; then subsequently characterized using scanning X-Ray Photoelectron Spectroscopy and small-spot spectroscopic ellipsometry.

Electron exposures utilized the electron beam from a Perkin-Elmer 10-155 Cylindrical-Auger Electron Optics System; calibrated and characterized using a ThorLabs DCC1645c camera in conjunction with a Ce:YAG scintillator. EUV exposures utilized the Synchrotron Ultraviolet Radiation Facility at NIST. We find that the carbon growth rates for both exposure methods have sub-linear pressure dependence at low irradiance which transitions to linear scaling at higher irradiance. The growth rates at which this transition occurs, however, are different for EUV and e-beam irradiation.

11:40am TF+PS-ThM12 Production and Characterization of Thin Film Group IIIB, IVB and Rare Earth Hydrides by Reactive Evaporation, *James Provo*, J.L. Provo Consulting

A recent short history of reactive evaporation by Mattox (1) described various methods for producing oxides, nitrides, carbides, and some compound materials using this special process. However, no mention was made producing hydrides using this method. A study was performed in the mid 1970's at the General Electric Company (GE) Neutron Devices Department (GEND) in Largo, FL, by the author to study preparation of thin film hydrides using reactive evaporation and to determine their unique characteristics and properties.

Films were produced of scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), and the rare earth praseodymium (Pr), neodymium (Nd), gadolinium (Gd), dysprosium (Dy) and erbium(Er) hydrides by hot crucible filament evaporation in atmospheres of deuterium and tritium gas. All metal vacuum systems were used and dedicated for this special processing. Thin film test samples ~ 5,000Å thick were prepared on half-inch diameter molybdenum disk substrates for each occluder material.

Loading characteristics (i.e., gas –to-metal atomic ratios), oxidation characteristics, film structure, and stress properties were determined and showed near maximum gas-to-metal atomic ratios, variable oxidation properties, platelet type film structures and minimum film stress levels as determined by a double resonator technique. Also, stress aging characteristics were determined for some hydride films prepared in a radioactive tritium gas atmosphere.

The timeless data obtained showed gas-to-metal atomic ratios varied from 1.8 to 2.0, surface oxide levels varied from ~ 80Å to over 1,000Å, and initial normalized differential (tensile) stress levels were (1.0 to 4.0) x 10^8 dyne/cm^2 for tritium loaded samples and (1.0 to 2.0) x 10^9 dyne/cm^2 for deuterium loaded samples. Tritium loading, however, had the undesirable characteristic of having to dispose of the internal processing system fixtures, but the method generally produced desirable thin films.

† Formerly, Principal Member of the Technical Staff at Sandia National Laboratories,

Albuquerque, NM (Retired).

(1) Mattox, D.M., "History Corner- A Short History of Reactive Evaporation", SVC Bulletin, p.50 –

51, Spring 2014.

12:00pm TF+PS-ThM13 Cathodic Cage Plasma Deposition of TiN and TiO₂ Thin Films on Silicon Substrate, *R.R.M. de Sousa*, IFPI, Brazil, *P.S. Sato*, UFSCar, Brazil, *B.C. Viana*, UFPI, Brazil, *C. Alves Jr*, UFRSA, Brazil, *A. Nishimoto*, Kansai University, Japan, *Pedro Nascente*, UFSCar, Brazil

A new technique called cathodic cage plasma deposition (CCPD) was used for growing TiN and TiO₂ films on silicon substrate. In this technique, the samples are positioned inside a cage having uniformly distributed round holes with fixed diameter, and onto an alumina insulator disk, so that the plasma acts on the cage and not on the sample surface, eliminating possible defects usually formed during the conventional plasma deposition. The CCPD technique produces films with high uniformity and permits a good control of roughness and crystallinity. The main advantages of this technique are the uniformity, tri-dimensionality, and high rate of deposition of the deposited films, as well as low cost of production.

TiN coatings increase the surface hardness and decrease the friction coefficient, thus enhancing the lifetime of components and tools employed in the metalworking industries. Thin films of TiO₂ have attracted considerable attention because of different applications on many fields due to their unique properties, such as chemical stability, no toxicity, low cost, high refraction index, high permittivity, wide valence band, etc. The TiO₂ main crystalline phases are: anatase, brookite, and rutile. The TiO₂ thin films can have a mixture of these phases showing hybrid properties. Many studies have focused on relationship of the different phases as dependent of the deposition method and parameters. Each one of these phases has its own characteristic properties, leading to different applications.

In this work, the influence of the parameters (temperature and gas atmosphere) in the characteristics of the deposited films was investigated.

The TiN and TiO_2 thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy in order to identify their crystalline phases and estimate their thicknesses. The combination of XRD and Raman spectroscopy results indicates that only a TiN crystalline phase was detected for the TiN films, and mainly the anastase phase was detected for the TiO_2 film. High crystallinity and uniformity of the films were observed by XRD, Raman, and SEM, confirming that this low cost technique is effective in producing high quality TiN and TiO_2 films.

Thursday Afternoon, November 13, 2014

Manufacturing Science and Technology
Room: 302 - Session MS+PS+TF-ThA

Functionalization of Paper and Textiles & Their Applications
Moderator: Jack Rowe, North Carolina State University, Bridget R. Rogers, Vanderbilt University

2:20pm **MS+PS+TF-ThA1 Vapor-Phase Infiltration of Cellulose and Cotton**, *Mato Knez, K. Gregorczyk, M. Garcia, I. Azpitarte,* CIC nanoGUNE, Spain*, D. Pickup, C. Rogero*, Centro de Física de Materiales (CSIC-UPV-EHU), Spain **INVITED**
There is a significant interest in using inexpensive biological materials as substrates and scaffolds for emerging applications due to their natural occurrence. Of particular importance is the use of paper based materials and substrates for potential applications in energy storage, catalysis, solar cells, etc. Atomic layer deposition (ALD) has been proven to be the technique of choice to modify paper and other cellulose based materials due to its low reaction temperatures, extreme thickness control, and conformality. Furthermore, vapor phase infiltration techniques, which are a recent modification to ALD, have allowed infiltration of metal-organic precursors into a variety of organic materials including spider silk, porphyrins, and polytetrafluoroethylene (PTFE), leading to a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors, as-well-as surprising changes in bulk properties. Understanding the chemical interactions between precursors and substrates are crucial in order to approach applications. We modified cellulose and cotton with common ALD precursors and monitored the chemical changes after the reaction a semi-*in-situ* XPS experiments. Our findings show that the precursors induce small, but important changes to the biopolymer upon chemical interaction and that the precursors indeed react different to each other. The experiments also compare well to the final results of standard *ex-situ* XPS. Changes in the bulk mechanical properties of the substrates were studied through use of tensile testing. The ultimate tensile strength (UTS), Young's modulus (YM), and toughness are shown to be a non-linear function of both the precursor used and the number exposure cycles.

3:00pm **MS+PS+TF-ThA3 Patterned Photoreduction of Metal Atoms on Polymeric Substrates for Flexible Electronic Applications**, *Halil Akyildiz, J.C. Halbur,* North Carolina State University*, A.T. Roberts,* Redstone Arsenal*, H.O. Everitt,* Duke University*, J.S. Jur*, North Carolina State University
Flexible electronics are of interest for displays, sensors, and health monitoring systems. Polymeric substrates, being flexible, easy to manufacture and inexpensive, are wanted for such applications. However, polymers, aside from good properties usually require alteration of electronic and optical properties. Sequential vapor infiltration (SVI) is a technique that modifies polymer properties by formation of hybrid materials via infiltration of organometallic precursors into bulk polymers. In this work we present how SVI tailors the optical properties of polyethylene terephthalate (PET) fibers by infiltration of trimethylaluminum (TMA) precursors to form PET-Alumina hybrid structures. Photoluminescence (PL) spectroscopy showed an order of magnitude increase in photoluminescence as compared to the pristine PET fibers which is attributed to the increased interactions between polymer chains by formation of alumina polymer coordination complexes. Furthermore metal ions out of a metal salt solution were reduced onto the modified substrates by photo catalytic effect. Patterned silver lines on PET fabric were successfully achieved by selective excitation of the fabric using a laser source showing promising results for integration of electronic devices.

3:20pm **MS+PS+TF-ThA4 Multifunctional Fabrics via Tungsten ALD on Kevlar**, *Sarah Atanasov, B. Kalanyan, G.N. Parsons*, North Carolina State University
Multifunctional materials combine two or more distinct capabilities into a single article unit. Kevlar is a high strength fiber used for personal protection and other mechanically demanding applications. Adding conductivity to Kevlar creates a new multifunctional protective/electronic material for electromagnetic shielding, communications, and erosion resistant, anti-static fabrics and cables for space and automotive technologies. For this study, we coated Kevlar fibers and woven mats with ALD tungsten, using WF_6 and dilute silane (SiH_4, 2% Ar) at 220°C. Kevlar's thermal stability makes it a very amenable polymer for ALD coating at relatively high temperatures. Before W ALD, we deposited a TiO_2/Al_2O_3 bilayer by ALD onto the Kevlar, at various temperatures (50-220°C). The Al_2O_3 layer promotes W nucleation. The TiO_2 layer is important because previous mechanical analysis indicates that the TMA precursor degrades the Kevlar polymer backbone, whereas TiO_2 ALD using $TiCl_4$ and H_2O was less damaging. XPS analysis confirms the presence of TiO_2, Al_2O_3 and W on the fibers after each coating step. After W ALD, the yarns and mats are highly conductive (~3000 S/cm) and remain flexible. Tensile testing shows that upon coating with 20 ALD cycles, the strength of the Kevlar decreases from 3.32 GPa to 3.02 GPa. The ability to create highly conductive Kevlar with mechanical strength within 90% of the original mechanical performance could open new areas of application for large area low temperature ALD processing.

4:00pm **MS+PS+TF-ThA6 Direct and Self-Assembly of Nanocellulose Cleaved from Fiber Cell Walls and Integration in Device Manufacture**, *Orlando Rojas*, North Carolina State University **INVITED**
We introduce our work related to the application of surface and colloid science in the development of cellulose nanomaterials. These efforts take advantage of the process by which nature assembles fibers in a highly hierarchical structure encompassing a wide range of sizes, from the nano to the meter scales. A number of materials cleaved from the cell wall have been the subject of intensive research, including, nanofibrillar cellulose and cellulose nanocrystals, i.e., defect-free, rod-like crystalline residues after acid hydrolysis of cellulose fibers. Interest in nanocellulose originates from its appealing intrinsic properties: nanoscale dimensions, high surface area, unique morphology, low density, chirality and mechanical strength. Directing their assembly back to different hierarchical structures is a quest that can yield useful results in many revolutionary applications. As such, we will discuss the use of non-specific forces to create ultrathin films of nanocellulose at the air-solid interface for applications in nanocoatings, sensors, etc. Assemblies at other interfaces will be introduced as means to produce Pickering emulsions. Methods common in biophysics and employed to control the packing density of nanocellulose at the air-liquid and air-solid interfaces will be presented. A convective assembly setup assisted by shear and electric fields will be discussed as a suitable method to produce highly ordered structures. Concepts related to piezoelectric cellulose nanocrystal films, organic-inorganic hybrid materials with magnetic and other properties. Overall, the prospects of such novel materials will be explained in light of the unique properties of cellulose and its nanostructured assemblies.

5:20pm **MS+PS+TF-ThA10 Van der Waals Materials on Nanostructured Paper -- Aqueous Gating and Sensing Application**, *Wenzong Bao, Z. Fang, J. Wan, L.B. Hu*, University of Maryland, College Park
We report the first aqueous transistors on a bilayer-structured paper with a nanoscale smoother surface. Such transistors have a planar structure with source, drain and gate electrodes on the same surface of paper, and the mesoporous paper is used as an electrolyte container. Such transistors are enabled by a bilayer-structured all-cellulose paper with nano-fibrilated cellulose on the top surface that leads to an excellent surface smoothness, while the rest of micro-sized cellulose fibers can absorb electrolyte effectively. Based on 2D Van der Waals materials such as graphene and MoS2, we demonstrate high-performance transistors with large on-off ratio. Our devices also show excellent bending flexibility. Such planar transistors with absorbed electrolyte gating can be used as sensors integrated with other components towards paper microfluidic systems.

5:40pm **MS+PS+TF-ThA11 Mechanistic Understanding of Anomalous Scaling Law of Mechanical Properties of Nano-Cellulose Paper**, *S. Zhu, Z. Jia, Y. Li, Z. Fang, S. Parvinian, N.J. Weadock, O. Vaaland, Y.C. Chen, L.B. Hu, Teng Li*, University of Maryland, College Park
The quest of both strength and toughness is perpetual in advanced material design; unfortunately, these two mechanical properties are generally mutually exclusive. A general and feasible mechanism to address the conflict of strength vs. toughness still remains elusive. Here we demonstrate an anomalous but highly desirable scaling law of the mechanical properties of cellulose nanopaper: both its strength and toughness increase simultaneously (40 & 130 times, respectively) as the size of the constituent cellulose fibers decreases (from a diameter of 27 microns to 10 nm). Our theoretical mechanics modeling and molecular dynamics simulations reveal the underlying mechanistic understanding of such an anomalous scaling law. These stimulating results suggest a fundamental bottom-up strategy generally applicable for other material building blocks, and thus hold the promising potential toward a new scaling law: the smaller, the stronger AND the tougher. There are abundant opportunities to utilize the fundamental bottom-up strategy to design a novel class of functional materials that are both strong and tough.

Plasma Science and Technology
Room: 308 - Session PS+SE-ThA

Atmospheric Pressure Plasma Processing; Fundamental and Applications

Moderator: Richard van de Sanden, DIFFER, Stefan Welzel, FOM Institute DIFFER

2:20pm PS+SE-ThA1 Insights into the Chemistry of Atmospheric Pressure Plasma Deposition Processes, *Fiorenza Fanelli*, Institute of Inorganic Methodologies and Plasmas - National Research Council, Italy, *P. Bosso, A.M. Mastrangelo, F. Fracassi*, University of Bari 'Aldo Moro', Italy **INVITED**
Over the last decade there have been considerable advances in the utilization of atmospheric pressure cold plasmas for thin film deposition. Intense research efforts have been made to develop a large variety of processes which exploit different types of atmospheric pressure discharges for the direct and remote deposition of thin films from monomers in gas, vapor and aerosol form [1]. However diagnostic studies of the plasma chemistry and mechanistic investigations of thin film growth are still scarce, while being crucial prerequisite for further process optimization. The research should be addressed to detect the film precursors, to identify the main reaction pathways (both homogeneous and heterogeneous processes) and to clarify the plasma-surface interaction.

In this contribution, our studies on thin film deposition by dielectric barrier discharges (DBDs) will be presented to provide insights into the chemistry of atmospheric pressure plasma processes. Examples discussed will include the investigation of the role of the monomer chemical structure in the plasma-enhanced chemical vapor deposition of organosilicon coatings from different methyldisiloxanes [2], and the study of the influence of air and water vapor feed gas impurities in the deposition of fluorocarbon coatings from argon-hexafluoropropene fed DBDs [3]. Our recent work on the deposition and characterization of organic-inorganic hydrocarbon polymer/ZnO nanoparticles nanocomposite coatings by a DBD fed with helium and the aerosol of a dispersion of oleate-capped ZnO nanoparticles in hydrocarbon solvents will be presented [4]. Results from the plasma jet co-deposition of acrylic acid and ethylene towards water-stable coatings containing carboxylic functionalities will be also shown.

The overall deposition mechanisms will be outlined on the basis of the results from the chemical and morphological characterization of the coatings, the optical emission spectroscopy investigation of the plasma phase, the analysis of the exhaust gas by means of gaschromatography-mass spectrometry. The latter is a powerful *indirect* diagnostic technique of the gas phase which allows the assessment of the monomer depletion and the quali-quantitative determination of stable byproducts formed by plasma activation.

[1] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naudé, N. Gherardi, *Plasma Process. Polym.*, 9, 1041 (2012).

[2] F. Fanelli, S. Lovascio, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.*, 9, 1132 (2012).

[3] F. Fanelli, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.*, 8, 557 (2011).

[4] F. Fanelli, A. M. Mastrangelo, F. Fracassi, *Langmuir*, 30, 857 (2014).

3:00pm PS+SE-ThA3 Understanding Charge Transfer Reactions at a Plasma-Liquid Interface, *Paul Rumbach**, University of Notre Dame, *R.M. Sankaran*, Case Western Reserve University, *D.M. Bartels, D.B. Go*, University of Notre Dame
The interaction of atmospheric-pressure plasma jets with liquids is becoming increasingly important for medical and materials applications. Despite empirical evidence of reactions occurring both in the bulk plasma and liquid phases, a basic understanding of the chemistry, particularly at the interface of the plasma and liquid, remains poorly understood. Previous studies have shown that species produced in the plasma phase such as nitric oxide (NO) and hydroxyl radicals (OH) can solvate in the liquid, yielding products such as nitrous acid (HNO_2) and hydrogen peroxide (H_2O_2) in the bulk solution [1]. In addition, we have recently shown that charge can be transferred from a DC microplasma jet into an aqueous solution to promote electrolytic reduction reactions [2]. However, it remains unclear how these charge transfer reactions occur and, in particular, if plasma electrons solvate in the liquid before subsequently reducing solution species.

To clarify the role of electrons solvating at a plasma-liquid interface, we have designed and built an experiment to detect solvated electrons using

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* Coburn & Winters Student Award Finalist

optical absorption spectroscopy. Electrons solvated in aqueous solutions are well known to absorb strongly in the red. Initial models suggest that because of the short lifetime of solvated electrons in aqueous solutions (~1 μ s) and anticipated solvation depths on the order $10 - 100$ nm, optical absorption will be on the order of one part in 10^6, making this an inherently challenging measurement. In this presentation, we will give an overview of our experimental method and present preliminary findings on direct measurements of electron solvation.

[1] P. Rumbach, M. Witzke, R. M. Sankaran, and D. B. Go, *J. Am. Chem. Soc.* **135** 16264-16267 (2013).

[2] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **45** 442001 (2012).

3:20pm PS+SE-ThA4 A Novel Atmospheric Pressure Plasma Application for Fuel Tank Inerting, *Matthew Price, A. Srivastava*, Interspace, Inc.
Aircraft fuel tanks have traditionally been protected from ballistic threats caused from explosive vapors by filling the area above the fuel with suppressant foam or inert gas. More recently fuel tank inerting systems have been developed for commercial transport aircraft. Inert gas is the preferred method since foam is heavy, reduces fuel tank capacity and is expensive to maintain. Current solutions consist of Onboard Inert Gas Generation Systems (OBIGGS) to reduce oxygen content in fuel tanks through the use of nitrogen-air separators. These membrane-based separators require high-powered pumps to flow air through small pores in the membranes. OBIGGS systems are bulky and too power hungry to be practical for smaller aircraft with multiple fuel tanks and limited electrical power. INTERSPACE has developed an innovative and efficient inerting system that does not rely on a pre-stored inerting agent or bleed air and is scalable to support multiple independent tanks. The system requires minimal electrical power and is capable of inerting to trace oxygen concentration levels without contaminating the fuel.

Our solution uses a getter material to readily sequester oxygen as surface oxides. A non-thermal, atmospheric pressure plasma then combines hydrocarbons in the tank with the getter to reduce the oxide and reverse the process to form water vapor. No consumable inerting product is used. Experimental data shows the getter absorbs 20 times its volume in oxygen before saturation. Scaling up this reaction would inert a 500 gallon fuel tank in 11.4 minutes with one liter getter at standard temperature and pressure conditions. Time-to-inert decreases at higher altitudes due to lower pressure. Time-to-inert curves were calculated for the typical aircraft flight envelope based on this model. We have successfully demonstrated the feasibility of our inerting system in a laboratory environment. Our inerting system is highly selective to oxygen, and eliminates the membranes and high power pumps used in existing systems. The next step will be to evaluate a prototype system through demonstration testing on the replica of a military aircraft fuel tank system. A customized plasma source will be developed optimized in size and weight competitive with aircraft applications.

4:00pm PS+SE-ThA6 *In Situ* Diagnostic Studies of CO_2 containing Dielectric Barrier Discharges, *Stefan Welzel*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *F. Brehmer*, Eindhoven University of Technology; AFS GmbH, Germany, *B.L.M. Klarenaar*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM Institute DIFFER; Eindhoven University of Technology, Netherlands, *R. Engeln*, Eindhoven University of Technology, Netherlands
Carbon dioxide will be a key enabler for the integration of renewable energy into a future CO_2 neutral energy system as well as into chemical industry. The application of non-equilibrium plasmas offers a promising route to overcome the initial energy-demanding CO_2 dissociation step. Through subsequent hydrogenation of the CO produced, gaseous or liquid hydrocarbon(ate)s are synthesised. Dielectric barrier discharges (DBDs) are known as useful tools in plasma-assisted gas conversion. The main objective was to unravel main reaction mechanisms in CO_2 containing DBDs through combination of several *in-situ* diagnostic techniques.

Optical emission spectroscopy, (infrared) absorption spectroscopy along with rotational Raman scattering were employed to study the CO_2 conversion and deduce gas temperatures in mid-frequency (kHz) driven DBDs at elevated pressures. To study the kinetics of CO formation the DBD was additionally operated in pulsed mode. Absolute densities of CO, O_2 and O_3 were established downstream the plasma reactor. The CO yield was typically below 5% for gas flow rates that would allow reasonable throughput. The generally weak emission of electronically excited species (CO_2^+, CO) was monitored during individual AC cycles. Additionally, phase- and time-resolved signals of ro-vibrational absorption lines of CO and CO_2 in their (electronic) ground state were detected by quantum cascade laser absorption spectroscopy. In contrast to emission, the CO absorption remained constant throughout individual AC cycles. The

modulation of CO absorption signals during pulsed operation can be successfully modelled by considering the power density of the DBD, the reactor wall and gas temperatures (up to 550 K), and the residence time of the gas along with the reactor geometry.

The results suggest electron-impact CO_2 excitation and ionisation followed by potentially surface enhanced recombination. The stoichiometric $CO:O_2$ ratio is described by a uniform trend as function of the number of charges transferred during the residence time of CO_2 in the active plasma zone.

4:20pm PS+SE-ThA7 Effect of the Nature of the Plasma Gas on the Resulting Chemistry of Atmospheric Plasma Deposited Coatings and of Plasma Treated Gases, *D. Merche, N. Vandencasteele, A. Ozkan, J. Hubert, François Reniers*, Université Libre de Bruxelles, Belgium
In atmospheric plasma processes, the use of a main gas, usually considered as inert, to sustain the plasma is common. Nitrogen, argon and helium are the most regularly used gases. If the nature of the gas has a strong influence in the breakdown discharge voltage (due to Paschen Law), it also leads to plasmas which are optically and electrically different. This has drastic consequences on the chemistry and structure of plasma deposited coatings and on the chemistry of plasma treated gases. In this study, we compare, and try to explain, the results obtained on different topics using either argon or helium as main plasma gas.

All experiments have been conducted in dielectric barrier discharge reactors, powered with sinusoidal AFS generators, operating at frequencies lower than 40 kHz. For all the studies the reactors have been pumped down to evacuate contaminations and then backfilled with the plasma gas (Ar or He). The precursor is then injected in the DBD through the appropriate flow of the carrier gas.

Internal chemistry of coatings :

Through a combined XPS, FTIR and SIMS study, it is shown that the degree of cross-linking, the branching and the number of insaturations of plasma-polymerized polystyrene or sulfonated polystyrene (for fuel cell applications) is higher with argon than with helium, whereas the density of aromatics exhibits the opposite behavior.

Surface roughness of coatings

Similarly, for all the organic coatings synthesized by a dielectric barrier discharge (PS, CFx from C_6F_{12}, PA), the roughness, determined by AFM is always higher with argon than with helium.

Conversion of CO_2 by DBD

Finally, the conversion rate of CO_2 into CO in atmospheric plasma conditions (DBD), is higher when argon is the main plasma gas than with helium.

It is suggested that all these effects are strongly related to the plasma operating mode and to the energy distribution inside the plasma.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency

4:40pm PS+SE-ThA8 Diagnostics of an Atmospheric-Pressure dc Glow Plasma in Contact with Solution: Insight into Plasma-Liquid Interaction, *Koichi Sasaki*, Hokkaido University, Japan **INVITED**
The interaction between an atmospheric-pressure plasma and a liquid attracts much attention in conjunction with plasma-aided medical treatments and plasma-assisted agriculture. Major interests are the production and the transport of OH radicals in plasmas in contact with liquids. In this work, we examined the spatial distribution of the OH radical density in the gas phase of a dc glow plasma produced between a stainless-steel nozzle as the anode and electrolyte of NaCl solution as the cathode by laser-induced fluorescence (LIF) imaging spectroscopy. We were careful about the influence of collisional quenching and the rotational temperature in deducing the spatial distribution of the OH radical density from the LIF images.

The maximum rotational temperature was approximately 3000 K, which was observed in the plasma column in contact with the electrolyte surface. The frequency of collisional quenching was also high in the contacting region to the electrolyte surface, suggesting that the dominant quencher of the excited state of OH was water vapor. The absolute density of water vapor was evaluated from the quenching frequency and the rate coefficient of collisional quenching. It was found that the partial pressure of water vapor was more than five times higher than the saturated vapor pressure of water at room temperature.

The OH radical density was high in the neighboring region to the electrolyte surface, suggesting that water vapor produced from the electrolyte is the parent of OH radical. However, the peak of the OH radical density was separated from the electrolyte surface, and also the OH radical density on the electrolyte surface was not zero. It is noted that, if OH radicals are not reactive on the electrolyte surface, the decrease in the OH density toward

the electrolyte surface would not be observed. On the other hand, if OH radicals are too reactive in the gas phase, the OH radical density on the electrolyte surface would become zero (Note that the production of OH in the cathode sheath is negligible), and in this case we cannot expect the interaction of OH radicals with the electrolyte. The axial distribution of the OH density observed in this work indicates that the electrolyte surface interacts with OH radicals as their sink. In other words, OH radicals are lost on the electrolyte surface. A possibility of the loss process is recombination to form hydrogen peroxide and water. In addition, we can also expect the transport of OH radicals into the inside of the electrolyte.

5:20pm PS+SE-ThA10 Absolute Measurements of Short Lived Reactive Species in Cold Atmospheric Pressure Plasmas, *Deborah O'Connell*, *K. Niemi, J. Dedrick, S. Schroeter, J. Bredin, A. West, E. Wagenaars, T. Gans*, University of York, UK
Low temperature plasmas are emerging as an exciting development for therapeutics. The unique properties of cold non-equilibrium plasmas have enormous potential in disease therapeutics and plasma pharmacology as drug alternatives. Applications of these plasmas include surface sterilization and bacterial decontamination, biofilm inactivation, antimicrobial treatment in food preservation, wound healing, to cancer treatment.

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, hydroxyl radical, superoxide, singlet delta oxygen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. RONS are known to play a crucial role in biological systems, such as signalling, and generating oxidative damage to a variety of cellular components, which can ultimately lead to cell death. Plasmas have the advantage of delivering these simultaneously providing potentially superior processes.

Transport of the plasma components to the target is complex. In the core plasma production region a large, but defined, number of species can be created (including for example O, N, NO, O_2^-). As the plasma interacts with ambient air new reactions and components are formed. Upon interaction with either humidity or liquid layers on biological samples new species of varying lifetimes can be created (e.g. OH, H, H_2O_2, $ONOO^-$). Energy dissipation at these interfaces is important and to date unclear.

In order to understand the chemical kinetics and plasma-liquid-biological interaction mechanisms measurements of the relevant RONS are key. Measurements and simulations under this atmospheric pressure environment are challenging, primarily due to the multi-phase (solid, liquid, gas and plasma), strongly non-equilibrium with large gradients (e.g. in electric field), high collisionality, thus requiring extremely high temporal (picosecond to nanosecond) and spatial (microns) resolution.

Two advanced optical diagnostic techniques are applied, and will be presented, to measure absolute radical densities: Pico-second two-photon absorption laser induced fluorescence (ps-TALIF) and high-resolution synchrotron VUV absorption spectroscopy will be presented. Radicals measured in an atmospheric pressure plasma operated in helium with varying admixtures of oxygen, nitrogen and water vapour will be presented.

5:40pm PS+SE-ThA11 Recent Progress in the Diagnostics of Microwave Discharges for Optimization of CO_2 Dissociation, *Tiago Silva*, *N. Britun, T. Godfroid, R. Snyders*, University of Mons, Belgium
The increase in global emissions of carbon dioxide (CO_2) due to fossil-fuel combustion and other energy-related human activities is strongly related with the global warming issue. Due to this effect, the study of CO_2 dissociation process is a highly demanding topic, which requires attention and efficient solutions. Among the proposed strategies, one possible way to limit CO_2 emission is to use plasma technology to break the CO_2 molecule into oxygen (O) and carbon monoxide (CO), which can be later used for production of valuable chemicals, e.g. for the fuel synthesis (syngas).

Recently, energy-efficient powerful plasma-chemical systems have been developed based on microwave plasmas. These discharges are often generated using electromagnetic waves in the range of 300 MHz to 10 GHz, and can operate over a wide range of conditions of pressure and power. In particular, microwave surfaguide discharges (MSGD) where the gas flow in the discharge tube is perpendicular to the waves propagation, are proven to be good solution for an efficient molecular dissociation of di- or multi-atomic species [1].

In this work, the recent results on CO_2-containing MSGD operating at 0.9 GHz and 2.45 GHz in pulsed and continuous regimes are presented. The plasma is sustained in CO_2 and CO_2+N_2 flowing gas mixtures in a quartz tube crossing a copper waveguide. The microwave discharges are characterized in terms of various plasma parameters using various optical emission spectroscopy (OES) methods. In particular, the characteristic

plasma temperatures, such as the gas temperature (via CO rotational spectra), and vibrational temperature (via N_2 vibrational bands) are determined as a function of time at different axial positions along the gas flow in the discharge tube. The CO_2 conversion rate in the discharge volume, along with the measurements of plasma energetic efficiency of such conversion is performed by means of optical emission actinometry. The results of the time- and space- resolved OES measurements demonstrate a non-uniform dissociation rate of CO_2 along the gas propagation direction in the discharge. As a result, the dissociation degree can be substantially modified by varying the power balance and the composition of the gas mixture [2]. In addition, in order to get a complete picture of the process, gas chromatography measurements were performed in the post discharge region. The obtained integrated results allow better understanding the µwave plasma-based dissociation of CO_2.

[1] T. Godfroid, J. P. Dauchot and M. Hecq, *Surf. Coating Technol* **174-175** 1276-1281 (2003)

[2] T. Silva, N. Britun, T. Godfroid, R. Snyders *Plasma Sources Sci. Technol* **23** 025009 (2014)

Plasma Science and Technology
Room: 305 - Session PS-ThA

Plasma Processing of Nanoparticles and Nanomaterials
Moderator: Mohan Sankaran, Case Western Reserve University

2:20pm PS-ThA1 Raman Spectroscopy as Diagnostics for Size Distribution and Surface Chemistry of Remote Plasma Synthesized Silicon Nanocrystals, *I. Dogan,* Eindhoven University of Technology, Netherlands*, R. Gresback, T. Nozaki,* Tokyo Institute of Technology, Japan*, MauritiusC.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands
The possibility to realize advanced photon management in solar cells and ultrahigh capacity charge storage in Li-ion batteries with silicon nanocrystals (Si-NCs) have boosted the interest on them, thanks to their size dependent optical properties and surface reactivity. To promote the use of these properties of Si-NCs in solar cells and batteries in an optimized manner, particle size control and surface engineering are the critical requirements. Therefore, accurate analysis of the size distribution is essential to optimize the process parameters to reach an ultimate control on nanocrystal size, which raises the requirement of a suitable diagnosis and post-analysis route. The analysis technique to be used is expected to provide quantitative data of size and morphology related features in a fast and non-destructive manner. Common techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence spectroscopy (PL) are time consuming and only provide qualitative data of the size distribution especially when the Si-NC size distribution is not monodisperse, which is hardly achievable in most of the nanocrystal processing tools. Thus, these techniques are far from being considered as ideal tools for effective size analysis. Our aim in this work is to demonstrate that, Si-NCs with multimodal size distributions can be quantitatively analysed in a fast and non-destructive way by using Raman spectroscopy (RS). Free standing densely packed Si-NCs are synthesized in Ar/SiH_4 and $Ar/SiCl_4$ gas mixtures by using a remote expanding thermal plasma and a ultra-high frequency non-thermal plasma. Synthesized Si-NCs have a multimodal size distribution with peak sizes of 5 nm and 70 nm, respectively. Experimental Raman spectra are deconvoluted for separate analysis of the sub-distributions by using the size dependent phonon confinement model. Comparison of the extracted size distributions with the distributions obtained from TEM and PL show that RS provides highly reliable, quantitative information of size distribution and volume fraction. Analysis of the surface chemistry of Si-NCs is performed by depositing a monolayer of Si-NCs on a 10 nm thick Ag. Using a 514 nm laser enhances of the Raman signal by two orders of magnitude, which reveals the presence of $Si-H_x$, $Si-O_x$ and $Si-Cl_x$ bonds on Si-NC surface. In addition, disappearance of $Si-H_x$ signal with oxidation is observed. With this observation, we show that, Raman spectroscopy can be used for probing the surface chemistry of Si-NCs. These results propose that Raman spectroscopy has the potential to become a standard diagnostic tool for the size and surface chemistry analysis of Si-NCs.

2:40pm PS-ThA2 High Rate Production of Silicon Nanoparticles Through a Microwave Torch Production Process, *David Oakes, M.A. Costolo, J.D. Lennhoff,* Physical Sciences Inc.
Nanometer sized aluminum particles are currently utilized as an energetic additive in propellant, pyrogen, and explosives formulations. Nano-silicon

is potentially an attractive replacement for nano-aluminum in these applications since it has a similar energy density while being less sensitive, and thus safer to handle. In addition silicon forms a thin passivation layer which makes it a stable additive compared to aluminum which can oxidize in-depth. Incorporating nano-silicon into energetic formulations is currently limited by the high cost of the material which is generally formed in low production rate, batch processes.

This paper describes the development of a scalable, continuous (non-batch) high production rate method for nano-silicon utilizing a microwave driven plasma torch-based process. Silane (SiH_4) is injected near the throat of the supersonic output nozzle of the torch where it dissociates in the near atmospheric pressure nitrogen plasma formed by the microwave discharge. The local gas temperature in the torch plenum is approximately 2800 K which is sufficient to produce greater than 0.9 moles of silicon atoms for each mole of SiH_4 (>90% efficiency). The resulting silicon atom rich gas is rapidly quenched ($\sim 2 \times 10^8$ K/s) in a supersonic expansion into a vacuum chamber ($\sim$ 50 torr) producing the seed particles that then grow to 10 – 20 nm in approximately 0.1 ms. The process meets the criteria specified by Kodas and Frielander for producing monodisperse particles in a flow reactor by namely: 1) Separating seed particle production in the supersonic expansion from subsequent growth of the seeds downstream of the nozzle, 2) Providing a flat velocity profile in the growth region enabling a uniform residence time for the particles in the growth region, and 3) Utilizing a high velocity jet which results in a short residence time in the growth region to minimize particle agglomeration.

Growth conditions will be described that produce 6 g/min of 10 -20 nm diameter silicon particles with a 140 m^2/g surface area from a 2 kW microwave discharge. Material analysis will be described including SEM and TEM to assess the particle morphology and size distribution, single point and BET surface area measurements, and EDX, differential scanning calorimetry, and electrochemical performance to assess purity and energetic characteristics of the material. Future efforts will extend the growth region of the process to enable larger particle sizes and scale up the microwave system to 5 kW to enable 15 – 30 g/min production rates.

3:00pm PS-ThA3 Plasma-Produced Nanomaterials for Energy Recovery and Storage, *Lorenzo Mangolini*, University of California, Riverside **INVITED**
Despite being heavily utilized in industry, the unique capabilities of non-thermal plasmas with respect of materials processing have yet to be fully realized. In this talk we will describe our effort in understanding the nucleation and growth of silicon nanoparticles in non-thermal plasmas and we will discuss their application for energy-related applications.

Several research groups have focused on nanoparticle nucleation and growth in silane-containing plasmas. Yet a clear understanding of the correlation between plasma parameters and the properties of silicon particles is missing. There is no theory explaining how a non-thermal process can produce nanocrystals of a material with a relatively high melting point within few milliseconds of reaction time. We have performed *in-situ* FTIR measurements and aerodynamically extracted particles along the length of a flow-through reactor similar to the one described in [1], and have found that silane is rapidly consumed and converted into amorphous particles with size close to their final one. Crystallization takes place after the precursor is fully consumed and within few milliseconds. An independent measurement of the crystallization rate of small silicon particles [2] suggests that their crystallization kinetics exceeds that of bulk amorphous silicon films. Despite this the current models describing the plasma-nanoparticle interaction [3,4] cannot justify the substantial heating necessary to achieve crystallization in such short time. Results from our ongoing efforts in this area will be presented.

By leveraging the processing capabilities of non-thermal plasmas it is possible to provide improvements in the performance of devices that are relevant for energy-related applications. By sintering plasma-produced nanocrystals it is possible to fabricate bulk samples with precise control of grain size and grain size distribution. These samples show some of the lowest thermal conductivities ever reported for the case of bulk nanostructured silicon. This is a promising step towards the development of highly efficient waste-heat recovering devices that do not require alloying with expensive materials such as germanium. Furthermore, plasma-produced silicon particles can also be integrated into anodes for lithium-ion batteries. Their excellent dispersibility into polymer matrices allows achieving stable operation over hundreds of charge-discharge cycles.

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4:00pm PS-ThA6 Atmospheric-Pressure Microplasma Synthesis of Colloidal Metal Nanoparticles, *Caroline De Vos, J. Baneton, J. Dille, S. Godet,* Université libre de Bruxelles, Belgium, *M. Sankaran,* Case Western Reserve University, *F.A.B. Reniers*, Université libre de Bruxelles, Belgium
Microscale plasmas are electrical discharges where at least one geometrical dimension is sub-millimetric. In consequence, they present a remarkable stability at high pressure as reducing the size of the plasma allows keeping breakdown voltages sufficiently low to avoid the glow-to-arc transition. [1] The development of non-thermal atmospheric pressure microplasmas facilitates the coupling with the liquid phase and offers new potential applications in water treatment, medicine and material synthesis. [2]

This study focuses on the synthesis of silver and gold nanoparticles in aqueous solution. The plasma, supplied with argon, is initiated at the surface of silver nitrate or chloroauric acid solution. The electrons from the discharge lead to electrochemical reactions and reduction of the metal cations. Different stabilizers such as polyvinyl alcohol and sodium dodecyl sulfate are mixed with the solution to prevent uncontrolled particle growth.

X-ray photoelectron spectroscopy (XPS) spectra exhibit the metallic nature of the Ag and Au nanoparticles and particles growth is monitored by ultraviolet-visible absorbance spectroscopy. The two plasmon bands, characteristic of spherical Ag and Au nanoparticles, can be observed at 415 and 530 nm respectively. The morphology and the size of as-grown colloidal metal nanoparticles are evaluated by transmission electron microscopy (TEM). For silver nanoparticles, the average size rises from 10 to 20 nm when the discharge current increases from 2 to 5 mA. Moreover, bigger nanoparticles are observed at higher concentration and reaction times. For gold experiments, particles about 10 nm in diameter are synthesized at higher current than for silver experiments. Lower precursor concentration is necessary to avoid aggregates formation. In both cases, particles below 20 nm are spherical whereas at larger diameters, various shapes such as triangle, hexagon, appear.

In the project continuity, a comparison of the reduction mechanisms is performed for the two studied metals. At first, the proportion of reduced metal cations is quantified by potentiometric analyzes. Thereafter, the active species involved in the reduction process (e.g., H_2O_2, electrons) are discriminated. Finally, a bimetallic synthesis is studied to help the comprehension of the fundamental mechanisms. Indeed, metal ratio and alloy formation provide information about the reduction kinetic of both metals.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency.

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4:20pm PS-ThA7 Gas Chromatography and Mass Spectrometry Characterization of Nanoparticle-Producing Atmospheric-Pressure Microplasmas, *Jonathan Cole, R.M. Sankaran*, Case Western Reserve University
Plasma processes are becoming increasingly important for the production of nanoparticles by homogeneous nucleation.[1,2] The high-purity conditions that have made plasmas essential for thin film etching and deposition in the semiconductor industry similarly allow nanoparticles to be synthesized without organic stabilizers or other types of contaminants. In addition, high temperature and/or pressure materials such as silicon and diamond can be produced in plasmas because of non-equilibrium conditions. A novel class of plasmas for nanoparticle synthesis is microplasmas. Microplasmas operate stably at atmospheric pressure as a result of pd scaling (p being the gas pressure and d the electrode gap), eliminating the need for vacuum infrastructure. In addition, particle nucleation, growth, and agglomeration are controlled by the rapid quenching that results from the small volume and flow-through geometry.

Here, we present gas chromatography and mass spectrometry measurements of atmospheric-pressure microplasmas with reaction chemistries relevant to nanoparticle synthesis by homogeneous nucleation. We focus on two different gas chemistries that are used to produce nanoparticles: 1) metal-organic vapors that allow the synthesis of metal nanoparticles, such as Ni and Fe, and 2) hydrocarbon gases that allow the synthesis of carbon nanoparticles, including nanodiamonds. Measurements are performed on the effluent at the exit of the microplasma. To sample gases at high pressure (>1 atmosphere), we have built a mass spectrometry system consisting of an open ion source, quadrupole trap, 1-300 AMU detection range RGA (Dycor Technologies, Ltd.) and capillary inlet. The gas chromatography system (Shimadzu, Inc.) is equipped with a recently developed barrier ionization discharge detector, which is capable of universal detection of molecular gases with sensitivity at the ppm and ppb levels. The results are thus comprehensive, but restricted to the neutral vapor or gas molecule reaction

products because of the high sampling pressure. Important insight is nonetheless obtained about reactant conversion, gas product selectivity, process efficiency, and influence of plasma characteristics. The gas chemistry studies are complemented by optical emission spectroscopy (Ocean Optics, Inc.) and scanning mobility particle sizer spectrometry (TSI, Inc.) of the nanoparticle aerosol. Materials analysis of collected product by high resolution transmission electron microscopy is also carried out in support of the in situ measurements.

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U. Kortshagen, J. Phys. D 42, 113001 (2009).

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4:40pm PS-ThA8 Top-down InGaAs/GaAs Nanopillars Fabrication using a Bio-Nano-Process and a Neutral Beam Etching Process, *Cédric Thomas, K. Yoshikawa, C.Y. Lee, Y. Tamura, A. Higo,* Tohoku University, Japan, *T. Kiba, A. Murayama,* Hokkaido University, Japan, *I. Yamashita,* Nara Institute of Science and Technology, Japan, *S. Samukawa*, Tohoku University, Japan
Quantum dot (QD) lasers have been extensively studied in the last few decades due to their device characteristics benefits. However, fabrication of a high density and uniform two-dimensional array of QDs is still a big challenge. We have developed a damage-free top-down process for creating InGaAs QDs by combining a high-density bio-template [1] and a neutral beam (NB) etching process [2]. The bio-nano process consists of a high-density (up to 7×10^{11} cm^{-2}), two-dimensional array of cage-shaped proteins called ferritins with encapsulated metal oxide nanoparticles (NPs). Ferritins can be functionalized with polyethylene glycol (PEG) to control distance between them and avoid QDs in-plane coupling. After removal of the protein shell, 7 nm in diameter iron oxide NPs were used as etching masks. The NB etching consists of an inductively coupled plasma chamber separated from the process chamber by a carbon electrode with a high-aspect-ratio aperture array. As a result, the charged particles are efficiently neutralized whereas almost no UV photons can reach the sample.

A self-assembled monolayer of PEG-ferritins was formed by spin coating on a GaAs cap surface with native oxide. Samples grown by metalorganic vapor phase epitaxy (MOVPE) with the following structure were used: 10-nm-thick GaAs cap, three 8-nm-thick $In_{0.24}Ga_{0.76}As$ active layers separated by two 20-nm-thick GaAs barrier layers on top of a semi-insulating substrate. A low-temperature oxygen annealing in vacuum was used to remove protein shell and form etching mask with the iron oxide cores. Subsequently, a hydrogen radical treatment was performed during 30 min at 350°C to remove native oxide, followed by hydrogen passivation at room temperature. Nanopillars were etched by neutral beam etching process with a mixture of argon and chlorine. Substrate temperature, neutrals energy and mixture ratio were investigated to find the optimized conditions in term of etching profile and nanopillars density. It has been found that a mixture ratio of Ar:Cl$_2$ = 27:73 with a substrate temperature of 50°C were the best conditions to obtain high-density and anisotropic nanopillars, with diameters about 20 nm and height about 80 nm. After regrowth of the GaAs barrier layer by MOVPE, photoluminescence was observed. PL emission from InGaAs QDs could be detected. The results showed that III-V compound QDs can be realized by this damage free top-down nanoprocess.

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5:00pm PS-ThA9 Nanostructuring of Metal Surfaces by Low Energy He Ions, *Irem Tanyeli*, FOM Institute DIFFER, Netherlands, *L. Marot,* University of Basel, Switzerland, *M.C.M. van de Sanden,* FOM institute DIFFER, Netherlands, *G. de Temmerman*, ITER Organization, Netherlands
The effect of low energy (<50 eV) helium ion irradiation on surface modifications of metals has been studied [1,2]. The most pronounced works have been done on tungsten and molybdenum surfaces [2]. Nanostructure formation on these surfaces by high fluxes of low energy helium ions is identified as a self-growth process of He bubbles. In this study, we provide a size-controlled nanostructure formation by surface temperature and plasma exposure time on iron surfaces consistently with the experiments on tungsten and molybdenum. Besides, various metal surfaces such as titanium, aluminum and copper are irradiated by low energy He ions. We investigated the behavior of these surfaces under the He ion irradiation as a function of surface temperature, plasma exposure time and He ion flux. Different surface morphologies are observed for these metals. Nanostructure growth kinetics shows dependency on surface temperature and plasma exposure time. It has been shown that the nanostructured surfaces present high surface area and hence high light absorption [3]. The photo-catalytic activity of our metal surfaces will be presented.

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5:20pm PS-ThA10 Nucleation of Microcrystalline Silicon Thin Films on Nano-Imprint Textured Substrates, *Jurgen Palmans*, *T. Faraz, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, Netherlands

Hydrogenated microcrystalline silicon (μc-Si:H) is important in thin-film silicon solar technology where it is combined with amorphous silicon (*a*-Si:H) in tandem cells for enhanced light absorption. However, efficient light absorption requires thick (>1 μm) μc-Si:H films compared to thin *a*-Si:H (~350 nm). Since reduced absorber thickness is desired, the potential of light management, typically induced by texture-etched transparent conductive oxides (TCO), has been explored, demonstrating a strong dependence of absorber layer quality on TCO chemical nature and morphology. Generally, electrical, optical and structural properties require optimization. Due to parameter interdependence, nano-imprint lithography (NIL) was introduced to decouple electrical/optical and structural properties by inducing texture on glass prior to TCO deposition, allowing independent optimization of light diffraction and electrical/optical requirements. The potential of NIL textures has been demonstrated in this respect. However, such novel morphologies (periodic/random) impact absorber layer quality. Therefore, the nucleation of μc-Si:H thin films (~100 nm), deposited under high power-high pressure conditions in a capacitively coupled plasma reactor, has been studied on various NIL textured substrates. To replicate a solar cell structure, NIL textured and flat glass have been coated with ~500 nm magnetron sputtered aluminum doped zinc oxide (AZO). Characterization through Raman spectroscopy and crystal grain analysis has been performed. For flat glass, the crystalline volume fraction (X_c) increased a factor 2 upon AZO addition joined by a narrower phase transition. This was related to a different microstructure evolution. Introducing a NIL texture increased nucleation delay on randomly textured compared to periodically textured substrates. Since nucleation depends on process conditions, i.e. silane flow rate (Φ_{SiH4}), the role of ions and radicals is considered a determining factor. A reduced Φ_{SiH4} enhances the ion-to-growth flux ratio and ion energy, promoting surface diffusion[1]. However, on rough morphologies the ion contribution per unit area is reduced, therefore reducing X_c on NIL substrates. When shifting to the phase transition, preferential etching of *a*-Si:H by atomic hydrogen dominates while the ion contribution is reduced. This is confirmed by the microstructure parameter (R*) experiencing a transition from void-rich to (di)vacancy-dominated films. Furthermore, a direct correlation of R* and X_c was obtained. The insights obtained as such directly impact process control when dealing with challenging morphologies.

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5:40pm PS-ThA11 Synthesis of AZO Film on Polymer by Nano-Process Control with Confined Magnetic Field Sputtering, *J.G. Han*, NU-SKKU Joint Institute for Plasma-Nano Materials, Republic of Korea, *Subong Jin*, *B.B. Sahu, J.B. Kim*, NU-SKKU Joint institute for plasma nano materials, Republic of Korea, *K. Takeda, M. Hori*, Plasma Nanotechnology Research Center, Japan

Al doped ZnO(AZO) film has been attracting as one of promising candidate film replacing ITO film for transparent conductive oxide film of next generation flexible digital electronics devices. The relatively low resistivity and transparency of AZO film deposited at low temperature are still hurdles to overcome for replacing ITO film even though its unique advantages in low cost and high toughness over those of ITO film. It is well known that resistivity is closely associated with carrier concentration and mobility which are controlled by stoichiometry, binding energy of atoms and lattice defects of film including oxygen vacancy as well as Al replacement in Zn atom sites.

The control of those atomistic structure and lattice defects is affected by surface energy accumulated with atoms and molecules deposited at top surface layer during film nucleation and growth depending on process parameters during deposition process. The surface energy is mostly comprised of kinetic energy of neutrals, electronic energy of activated neutral molecule and atoms and ions as well as flux density. We have investigated effect of those atomic and molecular level energy analysis on structure formation and related electrical property changes by in-situ diagnostics during sputtering process under confirmal confined magnetic field. The kinetic energy and flux of sputtered atoms are controlled by independent variation of power density for direct sputtering and in-direct sputtering targets on polymer substrate at low temperature below 100 C. Optical emission spectroscopy and radical diagnostics as well as Langmuir probe analysis have been performed to measure plasma parameters. Carrier concentration and mobility have been analyzed depending on microstructure changes including binding energy of atoms and Al replacement of Zn site etc.. The resistivity is significantly reduced with

atomic level nano process control and can be reached less than 4E-4 at low temperature.

This paper discusses on fundamental mechanism of film nucleation and growth with top surface energy accumulation with atomic and molecular energy diagnostics for AZO film synthesis by magnetron sputtering, and then illustrate control of resistivity associated with control of carrier concentration and mobility.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 315 - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomemetic Materials
Moderator: Sally McArthur, Swinburne University of Technology, Adoracion Pegalajar-Jurado, Colorado State University

2:20pm SM+AS+BI+PS-ThA1 The Chemistry of Plasma Modified 3D Biomaterials, *Eloisa Sardella*, CNR-IMIP, Italy **INVITED**
Plasma processing has become a most powerful and versatile tool for surface functionalization of porous materials in biomedical field.

Non equilibrium plasmas have many advantages over wet chemistry approaches: they are highly eco-friendly, have high potentialities in developing surfaces with peculiar characteristics, are capable to be part of in-line material processing and most importantly, can be applied to any material. Consequently, it has opened many new opportunities for investigation of surface modification in various fields like tissue and organ regeneration and biosensing. In this talk, we shall give a brief review on the recent developments of plasma processing of porous materials. We shall describe our experience on non-equilibrium plasmas to modify materials of biomedical interest like: scaffolds for tissue engineering and 3D carbon nanotubes carpets for bio-sensing. This research is aimed to gain new insights on the potentialities of plasma processing of biomedical materials. This work is encouraged by a deep characterization of material's surface and investigation of the material/ bio-environment interface.

3:00pm SM+AS+BI+PS-ThA3 Advantages of Plasma Polymerized Surfaces for Cell Sheet Engineering over Other Deposition Techniques, *Heather Canavan*, *M.A. Cooperstein*, University of New Mexico, *B. Bluestein*, University of Washington, *J.A. Reed*, University of New Mexico **INVITED**
Poly(N-isopropyl acrylamide) (pNIPAM) undergoes a conformation change in a physiologically relevant temperature range: it is relatively hydrophobic above its lower critical solution temperature (LCST, ~32oC), and mammalian cells are easily cultured on pNIPAM-grafted surfaces. When the temperature is lowered below the LCST, the polymer's chains rapidly hydrate, and cells detach as intact sheets capable of being used to engineer tissues ("cell sheet engineering"). This behavior has led to a great deal of interest from the bioengineering community, resulting in a variety of film deposition methods, substrate storage techniques, and cell release methods. Unfortunately, this has also resulted in widely varying responses (e.g., % of cells released, biocompatibility and stability of surfaces, etc.) from the resulting cell sheets. In this work, we present a comprehensive comparison of the surface chemistry, biocompatibility, and effect on reversible cell adhesion that results from pNIPAM substrates fabricated using the most common polymerization (free radical and plasma polymerization) and deposition (spin coating and plasma polymerization) techniques. The relative biocompatibility of different mammalian cells (e.g., endothelial, epithelial, smooth muscle, and fibroblasts) was evaluated using appropriate cytotoxicity tests (MTS, Live/Dead, plating efficiency). The pNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using X-ray photoelectron spectroscopy and goniometry. We find that plasma polymerized NIPAM substrates (ppNIPAM) are more stable under a variety of storage conditions prior to their use. Furthermore, when used for cell culture, ppNIPAM films exhibit no cytotoxicity toward any of the cell types tested and yield excellent cell detachment (~85%), which is an important consideration for their ultimate use in engineered tissues.

4:00pm SM+AS+BI+PS-ThA6 Biofunctionalization of Surfaces by Energetic Ion Implantation: Fundamentals and Recent Progress on Applications, *Marcela Bilek, A. Kondyurin, E. Kosobrodova, G. Yeo*, University of Sydney, Australia, *S. Wise*, Heart Research Institute, Australia, *N.J. Nosworthy, C.G. dos Remedios, A.S. Weiss, D.R. McKenzie*, University of Sydney, Australia **INVITED**

Despite major research efforts in the field of biomaterials, rejection, severe immune responses, scar tissue and poor integration continue to seriously limit the performance of today's implantable biomedical devices. Implantable biomaterials that interact with their host via an interfacial layer of active biomolecules to direct a desired cellular response to the implant would represent a major leap forward. Another, perhaps equally revolutionary, development that is on the biomedical horizon is the introduction of cost-effective microarrays for fast, highly multiplexed screening for biomarkers on cell membranes and in a variety of analyte solutions.

Both of these advances will rely on the availability of methods to strongly attach biomolecules to surfaces whilst retaining their biological activity. Radicals embedded in nanoscale carbon rich surface layers by energetic ion bombardment can covalently immobilize bioactive proteins [*Proc. Nat. Acad. Sci* **108**(35) pp.14405-14410 (2011)] onto the surfaces of a wide range of materials, including polymers, metals, semiconductors and ceramics . This new approach delivers the strength and stability of covalent coupling without the need for chemical linker molecules and multi-step wet chemistry. Immobilization occurs in a single step directly from solution and the hydrophilic nature of the surface ensures that the bioactive 3D shapes of the protein molecules are minimally disturbed.

This presentation will describe recently developed approaches that use energetic ions extracted from plasma to facilitate simple, one-step covalent surface immobilization of bioactive molecules. A kinetic theory model of the biomolecule immobilization process via reactions with long-lived, mobile, surface-embedded radicals and supporting experimental data will be presented. Progress on applications of this technology to create antibody microarrays for highly multiplexed, simple analysis of cell surface markers and to engineer bioactive surfaces for implantable biomedical devices will be reviewed.

4:40pm SM+AS+BI+PS-ThA8 Three-Dimensional Biopolymeric Scaffold Surface Modification Using Plasma Enhanced Chemical Vapor Deposition: The Effect of Functionality and Wettability on Cell and Bacterial Attachment, *Morgan Hawker, A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) bioresorbable polymeric materials, such as porous scaffolds made of poly(ε-caprolactone) (PCL), have desirable bulk properties for tissue engineering, wound healing, and controlled-release drug delivery applications. However, the surface properties (e.g., chemical functionality and wettability) are often undesirable for certain biomedical applications. Therefore, the ability to fabricate 3D materials with ideal bulk properties and customizable surface properties is a critical aspect of biomaterial development. Here, we demonstrate the deposition of conformal films throughout the 3D porous scaffold network using plasma enhanced chemical vapor deposition (PECVD). Resulting film properties can be tailored by using different precursor species. Octofluoropropane (C_3F_8) and hexafluoropropylene oxide (HFPO) precursors were chosen as model hydrophobic film PECVD systems, whereas a copolymerization system consisting of allylamine/allyl alcohol (allylNH/allylOH) precursors was chosen as a model hydrophilic, nitrogen containing PECVD system. To ensure the efficiency and reproducibility of the treatments, both the exterior and interior of the plasma treated scaffolds were characterized using contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) to assess changes in wettability, chemical functionality, and scaffold architecture in comparison to untreated scaffolds. C_3F_8 and HFPO PECVD on scaffolds resulted in fluorocarbon films on the exterior of the scaffold, and the extent of deposition throughout the scaffold's 3D structure was controlled by treatment time. The nitrogen content of the allylNH/allylOH films was tailored by changing the feed gas composition of the copolymerized films. After surface modifications, modified PCL scaffold surface interactions with cells and bacteria were assessed to confirm the relevance of these coatings for the biomedical field. We also explored the effect of different plasma treatments on cell adhesion/proliferation using both human dermal fibroblasts and endothelial cells, bacterial attachment, and biofilm formation using *Escherichia coli*.

5:00pm SM+AS+BI+PS-ThA9 Plasma Polymerized Bandages for Wound Healing, *Jason Whittle, L.E. Smith, T.L. Fernandez*, University of South Australia

Wound healing is a multi-billion dollar drain on healthcare systems around the work. This is particularly true in developed countries as they deal with aging populations and conditions such as vascular disease and diabetes.

More than 30% of the costs associated with treating diabetes can be attributed to management of chronic wounds. Dressings for the clinical management of wounds are constantly evolving to provide antimicrobial environments and optimal gas exchange, pH and hydration to facilitate wound healing. Ideally, the next generation of wound dressings will also provide a favourable surface for cell attachment, proliferation and migration to further promote the healing process. A number of approaches have been developed for healing chronic wounds, many of which involve culturing of explanted cells, or donor cells, and returning them to the wound site. In this paper, we have used plasma polymerisation to develop surfaces which influence the migration rate of primary cells (keratinocytes, fibroblasts and endothelial cells). A pro-migratory surface will enable cell transport into the wound bed. Earlier workers have concentrated on cell attachment as a key measurement of clinical potential, but we have observed that cell mobility exhibits a preference for different surface chemistry to attachment, and this preference depends on cell type. We show how plasma polymerization can be used to produce surfaces with controllable chemistry, and explore the effect of changing surface chemistry on the migration rate of primary fibroblasts and keratinocytes in vitro. We also investigate the effect of these surfaces on wound closure rate using an in-vitro wounding model based on an engineered skin composite. We also explore the application of plasma polymerized pro-migratory surfaces to electrospun scaffolds for use with deeper wounds.

Friday Morning, November 14, 2014

Plasma Science and Technology
Room: 305 - Session PS1-FrM

Plasma Sources
Moderator: Steven Vitale, MIT Lincoln Laboratory

8:20am **PS1-FrM1 Small High Density Plasma Sources for Focussed Ion Beam Applications**, *Rod Boswell*, Australian National University, Australia **INVITED**
Oregon Physics has developed the HyperionTM system of high brightness plasma ion sources which are now being used on Focused Ion Beams and TOF-SIMS around the world. These plasma sources are ten times brighter than present sources and reduce the time necessary for analysis from days to hours. They are also more reliable and can be focused down to smaller spots. The development of these sources, especially the optimization of the rf antenna design and extraction geometry will be described. Extraction of positive ions is used for reverse engineering on the nano-metre scale and negative ions are used for Time of Flight Secondary Ion Mass Scectroscopy (TOFSIMS).

SIMS uses beam of primary ions (typically O-) focused onto a target. Sputtered secondary ions are measured by mass spectrometer which can detect elements and their isotopes in the low parts per billion (10-9 or ng/g) range. Particles as small as a few 100 nanometres can be analysed.

Time of Flight (TOF)SIMS measures the time of arrival of the secondary ions at the detector, which depends on their mass yielding an extremely good high mass resolution. It can detect: cocaine in urine, benzodiazepines (eg. valium) in hair and gunshot residues in fingerprints even after strenuous washing! Additionally, TOF-SIMS can simultaneously detect cocaine in the presence of other drugs (i.e. flurazepam (a benzodiazepine hypnotic) and chlorpromazine (used for psychosis and heroin withdrawal) in urine. It is possible to relate the TOF-SIMS fingerprints to the evidence found at the crime scene, which can be considered as examination of forensic evidence transfer. Elemental composition of anthrax spores using TOF-SIMS has been carried out by Weber et. al. at LLNL. This is of use in assessing the origin of bio-weapons.

9:00am **PS1-FrM3 A Remote Microwave Plasma Source for Reactive Gas Generation**, *Xing Chen*, I. Pokidov, K. Wenzel, C.X. Ji, MKS Instruments, Inc.
A remote microwave plasma source has been developed for generation of activated gases, such as O, H, N and F. The plasma source comprises a dielectric tube surrounded by a conductive coil that serves as microwave antenna and cooling structure. A waveguide is coupled to a microwave cavity to guide the microwave energy into the plasma discharge tube. The electric field of the microwave energy is oriented such that microwave propagates along the conductive coil and deposits energy uniformly in the plasma tube. The plasma discharge tube can be made of quartz, sapphire, aluminum nitride or other dielectric materials to accommodate various gas chemistries. This paper characterizes the plasma source and its operation with O_2, N_2, H_2, H_2O, NH_3, H_2/N_2 and H_2/He gasses. Experimental measurements of plasma density and atomic gas flux of O, N, and H, using Langmuir probes, recombination probes and calorimetry, are presented. Typical plasma density is on the order of 10^{12} cm^{-3}. The plasma source operates in a broad range of power and gas flow conditions. The use of microwave plasma generation, combined with crystalline plasma tube materials, significantly reduces tube erosion and associated chemical and particle contaminations.

9:20am **PS1-FrM4 Mechanisms for Plasma Density Distribution Control using a Large Diameter Radial Line Slot Antenna Microwave Plasma Source**, *Toshihiko Iwao*, T. Hirano, A. Suzuki, Tokyo Electron Limited, Japan, *P. Ventzek*, Tokyo Electron America, *K. Ishibashi*, Tokyo Electron Limited, Japan
Microwave plasmas are frequently employed for etch, thin film deposition and surface activation for semiconductor or flat panel manufacturing. A major advantage of microwave driven plasma sources operating in the overdense regime or surface wave regime is that the plasmas in the high density source and lower density substrate contacting region may be well separated. This separation is useful for damage free or highly selective plasma process applications. The radial line slot antenna is an efficient microwave applicator for these process applications. Microwaves are radiated from a metal plate with a slot pattern adjacent to the dielectric top window. The electromagnetic field distribution and plasma density are controlled by optimizing the pattern. [1] Uniform plasma processes with the radial line slot antenna source have been demonstrated; however, it is

challenging to overcome the tendency of the substrate-contacting plasma to become center-dense in large volume reactors under the action of ambipolar diffusion at low pressure. In this presentation, we present the results of an investigation of the effect of antenna size on the plasma density distribution for a wide gap reactor. A concurrent experimental and simulation study reveal the importance of controlling the transport parameters in the downstream wafer-contacting region to overcome ambipolar diffusion. [2] In particular, we show how the source region plasma generation impacts the electron energy distribution function in the downstream region. Anisotropic features in the electron energy distribution function plays a critical roll in controlling the plasma uniformity which we demonstrate through plasma absorption probe measurements and simulations of plasma structure.

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9:40am **PS1-FrM5 The NEPTUNE Bipolar Source: A New Instrument for Surface Treatment Applications**, *Dmytro Rafalskyi*, A. Aanesland, LPP, CNRS - Ecole Polytechnique, France
In this work we present a recently patented and developed source of oppositely charged particles called "Neptune". The source accelerates simultaneously positive ions and electrons extracted from an ICP discharge. The produced broad beam is quasi-neutral with high directionality of all emitted charged particles, and as a result a dedicated neutralizer is redundant in this system. The source can be operated using any kind of working gas, such as Ar, SF_6, CF_4 etc. The simultaneous ion-electron extraction is realized using the RF self-bias effect in low-pressure plasmas. A double-grid ion optical system is RF-powered ensuring both efficient ion extraction and acceleration, and electron injection. In the extraction system ions are continuously accelerated in the RF sheath between the first (plasma/screen) and second grids, while the electrons are extracted periodically when the sheath collapses. Due to the fact that the extraction system is RF-powered via a capacitor, a DC current cannot flow between the extraction grids, and the total amount of ions and electrons escaping the plasma is the same. The first proof-of-concept of the Neptune source is demonstrated. First results of the beam measurements are reported, particularly in comparison with a traditional 2-grid ion source equipped with an external neutralizer. We show here that the Neptune source can be efficiently used for low-ARDE processes, as well as for other applications where the accelerated flows with high directionality of both kinds of charged species are required. It is demonstrated that the independent control of the ion flux and energy allows achieving bipolar beams generation in wide range of parameters. It is shown that the proposed ion-electron extraction technique reduces charging effects on the substrate. This work was supported by a Marie Curie International Incoming Fellowships within the 7th European Community Framework (NEPTUNE PIIF-GA-2012-326054) and by ANR under grant number ANR-2011-BS09-40.

10:00am **PS1-FrM6 Process Optimization by Phase Control in Multi-Frequency Capacitive RF Plasmas**, *Julian Schulze*, E. Schuengel, West Virginia University, *A. Derzsi, I. Korolov, Z. Donko*, Hungarian Academy of Science, Hungary
An overview of a novel method to control process relevant plasma parameters and particle flux-energy distribution functions in multi-frequency capacitive radio frequency (CCRF) plasmas is presented. Based on experimental, simulation, and modeling studies in different gases (Ar, H_2, SiH_4, CF_4) we demonstrate that the ion flux-energy distribution function at the substrate can be controlled separately from the ion flux by adjusting the harmonics' phases and amplitudes in a CCRF discharge driven by multiple consecutive harmonics based on the Electrical Asymmetry Effect. The quality of this separate control is significantly better compared to classical dual-frequency plasmas driven by two largely different frequencies. Adding more harmonics enlarges the control range. Tuning the ion energy by phase control in H_2-SiH_4 plasmas allows to control the morphology of deposited Si:H thin films. In large area CCRF plasmas radial inhomogeneities of the ion flux due to standing wave effects can be prevented by customizing the driving voltage waveform.

These optimizations of process control are based on a detailed scientific understanding of the non-local particle heating mechanisms in technological plasmas. Such mechanisms are complex and strongly depend on global control parameters such as the gas mixture, pressure, and voltage amplitudes. Differences of the electron heating mechanisms in electropositive and electronegative plasmas and their effects on process control will be discussed. In electronegative and/or dusty plasmas, e.g. operated in CF_4 or SiH_4, a novel heating mode, the Ω-mode, and novel coupling mechanisms between the driving frequencies are present and strongly affect process relevant plasma parameters. Moreover, resonance

phenomena such as the Plasma Series Resonance play a major role in multi-frequency CCRF plasmas driven by customized voltage waveforms at low pressures of a few Pa.

Existing processing reactors can be easily upgraded to use the method of phase control in multi-frequency plasmas by modifying the external RF supply only. No modifications of the reactor itself is required, but a detailed understanding of the plasma physics is needed to optimize plasma-surface interactions.

10:40am **PS1-FrM8** **Controlling the Flux of Reactive Species in Electron Beam Generated Plasmas**, *Scott Walton, D.R. Boris, E.H. Lock, S.C. Hernandez, Tz.B. Petrova, G.M. Petrov*, Naval Research Laboratory

Electron beam generated plasmas are characterized by high plasma densities ($> 10^9$ cm^{-3}) and very low electron temperatures (< 1 eV), making them well-suited for next-generation processing techniques where high fluxes of low energy ions are desirable. In this work, we focus on controlling the flux of reactive species incident to substrates located adjacent to magnetically collimated electron beam generated plasmas. In particular, we discuss strategies for regulating both the type and energy of the ions at the substrate surface. We use a suite of diagnostics including Langmuir and RF impedance probes along with a mass-resolved ion energy analyzer to show how various operating parameters can be changed to control both the bulk plasma properties and the ion flux at the surface. This work is supported by the Naval Research Laboratory Base Program.

11:00am **PS1-FrM9** **Ignition Delay in Electronegative Pulsed Dual Source Tandem Plasmas**, *Shyam Sridhar, L. Liu, D.J. Economou, V.M. Donnelly*, University of Houston

Control of the ion energy distribution (IED) is of utmost importance in semiconductor manufacturing. Pulsed plasmas can produce IEDs with small energy spread, necessary to enhance etching selectivity and minimize damage. However, the IED is broadened during the power-on period by capacitive-coupling, imposing an RF potential on the DC plasma potential. This can be eliminated with a Faraday shield but, with electronegative gases, it is not possible to ignite pulsed ICPs, since electron density rapidly decays when power is off, and re-ignition requires large electric fields produced by high-voltage capacitive coupling. Motivated by this problem, we have explored a "tandem" plasma system, where a continuous (auxiliary) ICP is injected through a grid into a pulsed (main) ICP. Using such a system, an ignition delay was observed in pulsed (period 1 ms) Cl$_2$ plasmas with a duty ratio (DR) ~ 60%. The ignition delay monotonically increased with DR to reach a maximum of 500 ms at DR ~99%. It was also observed that, for a given DR, the ignition delay increased by increasing the main ICP power or by decreasing the auxiliary ICP power. The ignition delay may be attributed to the low electron density in the main ICP, which decays to a value less than the density when the auxiliary ICP were operating alone. At low electron densities, power transfer efficiency is poor. The flux of seed electrons from the auxiliary ICP then acts to restore the electron density, thereby improving the power transfer in the main ICP and allowing plasma re-ignition. Similar results were also observed using other electronegative gases such as SF$_6$ and CF$_4$/O$_2$ mixtures.

11:20am **PS1-FrM10** **A Global Model for Ignition Delay of Pulsed Electronegative Plasmas**, *Lei Liu, S. Sridhar, D.J. Economou, V.M. Donnelly*, University of Houston

A Faraday shield can be employed to minimize capacitive coupling in inductively coupled plasmas (ICP), to obtain ion energy distributions with a tight energy spread. However, in the presence of a Faraday shield, it is challenging to operate a pulsed electronegative plasma with a long afterglow duration, as most of the electrons are lost, and re-ignition requires large electric fields produced by high-voltage capacitive coupling. Our experimental studies have shown that by using a dual plasma source, consisting of a main pulsed ICP in tandem with an auxiliary continuous wave ICP, Faraday-shielded pulsed plasmas in electronegative gases can be produced even with long afterglow duration (1000 µs). However, an ignition delay was observed with duty cycles >60%. A global (spatially averaged) model with chlorine chemistry was developed to describe the mechanism of ignition delay. The flux of charged species from the auxiliary ICP was included in both particle and energy balance equations. Predicted results of ignition delay for different duty cycles, auxiliary ICP powers and main ICP powers agreed with experimental observations. The observed ignition delay increasing with increasing duty cycle is counter-intuitive. One would expect that, as the duty cycle increases, and the afterglow time correspondingly decreases (for constant pulse period), the electron density at the end of the afterglow would be higher, making it easier to re-ignite the plasma, i.e., shorter delay time, in contrast to observation. Once the lower plasma power is off for > ~5µs it appears that there is a critical electron density in the lower plasma (n$_{cr}$), equal to or below the electron density when the upper (cw) plasma is operating alone (no power in the lower

plasma). When both plasmas are powered, the afterglow of the lower plasma keeps decaying for as long as the electron density is above n$_{cr}$. This is because the rate of plasma production is then lower than the rate of plasma loss. As soon as the electron density falls below n$_{cr}$, the rate of plasma production starts exceeding the rate of plasma loss, and the electron density starts increasing, eventually re-igniting the ICP. Now, the higher the duty cycle, the higher the electron density at the end of the afterglow, and the longer it takes for that electron density to decay to n$_{cr}$, resulting in longer delay times.

11:40am **PS1-FrM11** **Ion Energy Distribution Control Using Phase Locked Harmonic Drive**, *A. Zafar*, North Carolina State University, *Y. Zhang*, University of Michigan, *T. Kummerer*, North Carolina State University, *D.H. Clark*, Plasmatherm Inc., *M.J. Kushner*, University of Michigan, *D. Coumou*, MKS Instruments, *Steven Shannon*, North Carolina State University

Dual frequency RF power delivery has demonstrated the capability to increase the operating range of industrial plasmas including independent control of electron density and sheath bias and control of ion energy distribution function (IEDF) width. In this talk, we focus on the later demonstration and present a method for enhanced control of IEDF shape by utilizing a dual frequency drive where harmonic frequencies are employed and the relative phase of these two applied waveforms is controlled. We will show that by controlling both current ratio and phase angle, not only can the width of the distribution be controlled, the higher order moments (specifically distribution skew) can also be controlled, providing distribution functions that are either skewed toward the low energy peak of a typical bimodal RF driven IEDF or skewed toward the high energy peak. Experimental and simulated results will be presented for both dual frequency and three frequency configurations.

Plasma Science and Technology
Room: 308 - Session PS2-FrM

Plasma Surface Interactions II
Moderator: Ryan M. Martin, IBM T.J. Watson Research Center

8:20am **PS2-FrM1** **Enhancement of Surface Migration by Photoemission-assisted Plasma for Atomic-Scale Surface Smoothing**, *A. Saijian, Y. Kotanikawa, Y. Ohtomo, Shuichi Ogawa, Y. Takakuwa*, Tohoku University, Japan

As a novel tool of plasma ion beam techniques for surface smoothing, we have developed a photoemission-assisted plasma ion source (PAP) [1]. It has been confirmed that the Ar$^+$-PAP treatment has an effect to smooth mechanically grinded Al and Cu surfaces with an initial surface roughness (Ra(0)) of a few hundred nanometers [1]. To clarify the surface morphology changes by PAP ion source and understand the PAP ion source-surface interaction, in this study, Cu deposited on Si rare surface (Cu(200 nm)/Si$_R$) with Ra(0) ~13 nm, has been used for surface smoothing treatments. Plasma parameters have been measured by a cylindrical single Langmuir probe to better understanding the characteristics of the PAP.

In the experimental apparatus of PAP, a Xe excimer lamp with UV light ($\lambda = 172$ nm) was employed, leading to the order of 10^{12} photoelectrons/cm^2/s, which enabled us to generate uniformly glow discharge over 2-inch Si wafer at bias voltage V$_B$ of 200 V under Ar atmosphere with pressure of 300 Pa, and to increase a discharge current up to 10^{-6}-10^{-4} A at smaller V$_B$ than 200 V, which is referred to as Townsend plasma. According to the plasma potential measured by Langmuir probe, taking the energy loss due to elastic collisions between Ar+ ion and Ar atom into account, we estimated the E$_k$ of Ar ion upon the impingement with the substrate to be 10.7 and 0.79 eV for glow and Townsend discharge, respectively. Based on the estimated values of E$_k$, a surface flattening model of the dry planarization process is discussed.

When the Cu surfaces irradiated by the photoemission-assisted glow discharge plasma (E$_k$ = ~10.7 eV), and the photoemission-assisted Townsend discharge (E$_k$ = ~0.79 eV), the surface roughness was improved down to ~69.8% and ~54.5%, respectively. It indicated that the PAP has the ability to reduce the surface roughness down to atomic-scale under both discharge conditions. It has been reported that diffusion barrier of Cu atom via hopping or exchanging on Cu surface is 0.04 ~ 0.66 eV [2] and the threshold energy of Cu sputtering by Ar$^+$ is between 25~50 eV [3]. Therefore the enhancement of surface migration of Cu atoms is mainly responsible for the improvement of Ra in discharge conditions. Conclusively it is considered that the photoemission-assisted plasma works

as an ion source with E_k in the order of eV, which sufficiently makes the surface morphology improved due to the enhancement of surface migration.

Reference

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8:40am PS2-FrM2 Silicon Etching using CW, Synchronized Pulsed and Bias Pulsed Cl₂ Plasma, *Odile Mourey*, G. Cunge, C. Petit-Etienne, M. Darnon, P.D. Brichon, E. Despiau-Pujo, E. Latu-Romain, O. Joubert, LTM - MINATEC - CEA/LETI, France

The semiconductor industry is more and more challenged by the miniaturization of integrated circuits and the introduction of new devices architectures. Typical high density plasma show limitations in terms of anisotropy, selectivity and ion induced damages to etch stacks of ultrathin layers. New plasma technologies that provide an atomic level control of etching processes are now required and pulsed plasmas are promising candidates. In this work, we compare the performances of typical CW ICP plasma with synchronous pulsed plasma (ICP and bias power pulsed in phase) and bias pulsed plasma (ICP is CW and bias pulsed). In each case we use Cl₂ plasma to etch silicon and several parameters are monitored including etch rate, surface roughness, thickness of SiCl$_x$ reactive layer, ions flux and ions energy. We also investigate the importance of the surface preparation. Using atomic force microscopy, we show that (by contrast with CW plasmas) the surface roughness increases as a function of etching time in pulsed plasmas and that this worsens at small duty cycle. Preliminary results of molecular dynamic simulations suggest that this could be attributed to the modulation of the ion energy in pulsed plasma: in the OFF period radicals can attack the surface defect created by individual ions impacts during the previous ON period.

9:00am PS2-FrM3 Utilizing Absorption, Emission, and Fluorescence Spectroscopies to Elucidate the Energetics of Plasma-Surface Interactions, J.M. Blechle, R.B. Davidson, E.J. Sutor, *Ellen Fisher*, Colorado State University

Plasma-enhanced chemical vapor deposition (PECVD), plasma etching, and plasma modification of surfaces are integral to a range of technologies including microelectronics, optical or protective coatings and biomaterials. Many mechanistic details for plasma processing of these materials, however, remain unknown. Understanding surface interactions of plasma species provides critical molecular level information about plasma processing, especially at interfaces. In addition, power dissipation and energetics are also important for elucidation of mechanistic details in plasma-surface interactions. The imaging of radicals interacting with surfaces (IRIS) technique measures interactions of radicals during plasma processing of a variety of materials. This technique combines molecular beam and plasma technologies with laser-induced fluorescence (LIF) to provide information on radical-surface interactions during plasma processing. Furthermore, IRIS provides direct information on the energetics of plasma-generated radicals as well as for species scattering off of surfaces. IRIS data for species in PECVD and etching environments will be presented. We have also employed both time-resolved optical emission spectroscopy (TR-OES) and broadband absorption spectroscopy (BAS) to our plasma systems to further explore the gas-phase chemistry and gas-surface interactions. In particular, IRIS, TR-OES and BAS data on oxygen-containing systems (O atoms, OH radicals), fluorocarbon radicals (CF and CF2), , and nitrogen-containing molecules (NO, NH, NH2, CN) will be presented by comparing and contrasting these groups of molecules. Correlation of gas-phase data, surface analysis information, and plasma-surface interface reactions will also be presented to provide more comprehensive mechanisms for overall plasma polymerization processes.

9:20am PS2-FrM4 Transmission of Plasma-Generated Free Radicals through Dielectric Films, *Faraz Choudhury*, G. Sabat, University of Wisconsin-Madison, Y. Nishi, Stanford University, J.L. Shohet, University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to free radicals from the plasma that may adversely affect the chemical, mechanical and electrical properties of the films. Modern low-k dielectrics have highly porous structures (up to 50%) and interconnected pores provide pathways for reactive species to enter into the material making them more susceptible to damage. Previous work utilized simulations[1] to determine the free-radical density and doses from the processing plasma. Several techniques have been developed and tested over the years for radical measurements[2], but the methods do not provide a direct measurement of the free radical concentrations at the location of the sample during processing. A new technique, using fluorophore dyes, can detect free radicals in a processing

plasma and determine the their fluence at the surface of a sample during processing is investigated. The fluorophore used in this work is Alexa Fluor® 488. After reaction with reactive oxygen species (ROS), the bright green fluorescence (excitation/emission maxima ~490/515 nm) of the dye is significantly degraded. This degradation is measured using a fluorometer. The change in intensity of the fluorescence can be used to measure the free radical fluence from the plasma. This technique can also be used to determine the number of free radicals that can penetrate through a layer of low-k dielectric film as follows. Alexa 488 is placed under free-standing dielectric films such as SiO₂ and SiCOH of various thicknesses to determine the penetration depth of free radicals that are present in a typical processing plasma. Fluorescent dyes that selectively react with specific types of free radicals can also be used. In particular, we will use hydroxyphenyl fluorescein (HPF) that is a hydroxyl (OH) radical sensor. The change in fluorescence of this dye after plasma exposure can be used to determine the OH radical fluence from the plasma. I-V, C-V and TDDB measurements can also be made as a function of plasma exposure time to determine the extent of damage to the electrical properties of the films.

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9:40am PS2-FrM5 Gas-Phase Chemistry and Plasma Surface Interactions, *Matthew Goeckner*, University of Texas at Dallas **INVITED**

Plasmas have been used extensively in the semiconductor industry for almost half a century. However as processing has reached the production of nano-scale devices, development of industrially viable processes have become more difficult. In part this is because of all of the free parameters that exist in such plasmas. To overcome this economic issue, tool vendors and semiconductor companies have turned to complex computational models of processing plasmas. The accuracy of those models requires a thorough understanding of the links between gas-phase chemistry and surface processes. In this talk, we will give a brief overview of what is known about the links between the gas-phase chemistry and surface processes and what still needs to be understood.

10:40am PS2-FrM8 Plasma Induced Roughness Formation on Photoresist Examined by HBr Plasma-Beam Etching, Y. Zhang, *Makoto Sekine*, K. Ishikawa, K. Takeda, H. Kondo, M. Hori, Nagoya University, Japan

For highly precise patterning technologies in device fabrication, it is required to suppress roughness formations on photoresist (PR) polymers during plasma etching processes. The HBr plasma treatment called 'plasma cure' was proposed to reduce the roughness formation [1]. In the previous studies, by using a beam irradiation system, we reported the PR roughness formation in fluorocarbon plasma [2], and the effect on roughness suppression by HBr plasma cure [3]. In this report, we have extensively investigated the roughness formation mechanism on the PR for ArF photolithography by some surface analyses and power spectral density (PSD) of the roughness.

The photoresist roughness observed by the atomic force microscope (AFM) is characterized by two dimensional (2D) PSDs and the frequency distribution for a digitized height profile [4]. Average slope and roll-off frequency of PSD are characterized by frequency components, the high-frequency roughness [5]. We treated the roughness data for six samples: (a) initial (pristine), (b) after Ar plasma beam irradiation (Ar), (c) after Ar plasma beam irradiation followed by HBr plasma cure (Ar→HBr), (d) after HBr plasma cure (HBr), (e) after HBr followed by Ar plasma beam irradiation (HBr→Ar), and (f) after HBr followed by H₂ plasma beam and Ar plasma beam irradiation (HBr→H₂→Ar).

The PSD slopes were changed by each process. The Ar plasma beam irradiation affected higher-frequency roughness, i.e. fine roughness induced on the PR surface. Thus the ion bombardments affected the local fine roughness. In particular for (e), Ar irradiation after HBr cure, the higher-frequency roughness could be reduced. This indicates that the HBr cure possibly hardened the PR surface by crosslinking polymeric chains, and the behavior was observed apparently on the decrease of roll-off frequency. On

the other hand, the HBr cure after Ar irradiation, (c), increased lower frequency components of roughness compared with just Ar plasma beam irradiation, (b). We speculated that the Ar-plasma beam formed a crust layer on the PR surface with unrelieved stress and HBr cure may soften the bulk PR to relieve the stress and cause agglomeration of polymers at the size over 10 nm.

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11:00am PS2-FrM9 Novel Gases for Obtaining High Etch Selectivity of Oxide to Nitride for Contact Etch, *Vijay Surla*, L. Daniel, R. Gupta, V. Pallem, Air Liquide

Contact oxide etch is a critical process in developing the next generation integrated device fabrication. With the gate feature size scaling down, the aspect ratio of the features increases and contact oxide etch process becomes more challenging. Very high etch selectivities of Oxide to Nitride are required for contact etch, and there is an increasing need for finding new etch gases that can perform better than the traditional gases like C_4F_8 and additive mixtures used by the semiconductor industry. To this end, Air Liquide is actively working on finding novel etch gas chemistries and in this work, we present the performance of some of the promising etch molecules that offer high etch selectivity of oxide to nitride and mask for contact etch application.

From a new etch molecule design standpoint, there are key etch performance indicators for contact etch, the most important of which are the etch selectivity of oxide to nitride and the oxide etch rate. In this study, several novel fluorocarbons have been first tested systematically using dual CCP etch tool to find a correlation between the etch molecule (structure, and function), and its affect on the etch performance. The use of mass spectrometry as a diagnostic to qualitatively understand the plasma species, with a simple matrix analysis, is presented. Molecules are initially screened based on etch rate and selectivity of different planar films. Sidewall protection is important when etching these features, and so the polymerizing nature of etch gases is also investigated. Specifically, the role of ion energy and oxygen addition on controlling the rate of polymerization is studied in order to find the operating process window that yields high etch selectivity. The perfomance of the etch gases is finally tested on an oxide pattern structure with amorphous carbon as mask material. SEM cross-sections are presented to show the effect of etch gas on etch profile, mask selectivity and mask preservation. The new gases have demonstrated significant selectivity improvement in comparison to traditional etch gases.

11:20am PS2-FrM10 Dielectric Barrier Discharges: Statistical Analysis of Discrete Filaments and Multi-filament Dynamics, *Floran Peeters*, *R.F. Rumphorst*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM institute DIFFER, Netherlands

Dielectric Barrier Discharges (DBD's) are used on a large industrial scale and have been studied for more than a century, with increasing interest in recent years in the areas of materials processing, plasma medicine and solar fuels. DBD's in filamentary mode consist of many small, transient microdischarges with diameters of ~ 0.1 mm and durations on the order of several 10's of nanoseconds, distributed over the dielectric surface. We study the collective behaviour of many such filaments in air by using a fast analog circuit capable of measuring the conductively transferred charge per filament. By using a miniature planar DBD with a 7 mm^2 electrode area, we determine charge/filament distributions without significant overlap between filaments in time, even at high filament number densities of up to 200 filaments/cm^2/period. Contrary to previous work, we find that the charge/filament distributions are log-normal in nature. Furthermore, the distributions are independent of filament number density for a given DBD geometry. With conventional charge-voltage (Q-V) measurements, Lissajous figures are obtained for the miniature DBD, where the slope during a discharge period has a clear 'staircase' shape. Analysis of these Lissajous figures, for 8 different DBD geometries, reveals that filaments do not occur randomly within a discharge period, as is often assumed, but affect each other's moment of ignition. Using both measurement techniques, we infer that multi-filament discharge dynamics are regulated by residual conductivity of the gas near the surface of the dielectric, resulting in step-wise ignition of filaments as a function of applied voltage. The log-normal charge/filament distributions, on the other hand, develop from the locally trapped charges on the dielectric. We suggest that both mobile charges from residual conductivity and immobile trapped charges

need to be considered in models of DBD's, especially when converting data from the abundant single-filament models in DBD literature to real devices.

11:40am PS2-FrM11 Single Step Conversion of Metal/Polymer Films to Flexible, Electrically Conductive Patterns by a Scanning Atmospheric-Pressure Microplasma Process, *Souvik Ghosh*, R. Yang, A.C. Barnes, S. Rowan, C.A. Zorman, P.X.-L. Feng, R.M. Sankaran, Case Western Reserve University

Atmospheric-pressure plasmas are often used to modify the surface of thin polymer films because of their ability to carry out reactions at low temperature and add unique functionality via radical chemistry. Recently, polymer films containing metal components have been exposed to plasmas to convert dispersed metal cations to supported metal nanoparticles. [1,2,3]

Such materials may be of interest for emerging applications in organic electronics, photovoltaics, and medical devices. However, few studies have assessed the electrical conductivity which is critical to these technologies.

Here, we show that polymer films loaded with metal cations can be converted to electrically conductive surfaces by an atmospheric-pressure plasma process. [4] Films of polyacrylic acid are loaded with Ag cations by solution processing and doctor's blade casting technique. The films are exposed to an atmospheric-pressure microplasma jet so that by scanning the plasma across the surface, microscale patterns with ~300 μm line width are produced. Reduction to crystalline metal is confirmed by X-ray diffraction. Characterization of the films by scanning electron microscopy and energy dispersive spectroscopy reveals that plasma exposure results in nucleation and growth of aggregated Ag nanoparticles. Additionally, cross sectional images show that the formation of Ag is limited to near the surface (~5 μm). Electrical characterization of the films shows that the patterns are highly conductive with a bulk resistivity of ~1 mΩ-cm. To understand the mechanism for reduction, we compared our process with UV irradiation, heating, and laser treatment. None of these approaches produced similar reduction, crystallinity, or conductivity. We hypothesize an electrodiffusion model whereby Ag cations diffuse in the polymer film only in the presence of the plasma which creates an electric field through the film. This results in an enrichment of Ag cations at the surface. Reduction by the plasma then leads to a near-surface metallized layer. Thus, highly conductive surface patterns are generated from relatively low loadings of metal . References: [1] J. J. *et al.*, *Langmuir* **22**, 11388 (2006). [2] S. W. Lee *et al.*, *Adv. Func. Mater.* **21**, 2155 (2011). [3] S. W. Lee *et al.*, *Macromolecules* **45**, 8201 (2012). [4] S. Ghosh *et al.*, ACS Appl. Mater. Interfaces **6**, 3099 (2014).

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